Journal of Minerals and Materials Characterization and Engineering, 2021, 9, 480-498
https://www.scirp.org/journal/jmmce
ISSN Online: 2327-4085
ISSN Print: 2327-4077

Usability of a Natural Tuff as Admixture in Clinker and Its Influence on the Physico-Chemical and Mechanical Properties of Mortar

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How to cite this paper: Zerbo, L., Sawadogo, M., Sawadogo, Y., Salogo, S., Ouedrago, M., Seynou, M., Lecomte-Nana, G. and Blanchart, P. (2021) Usability of a Natural Tuff as Admixture in Clinker and Its Influence on the Physico-Chemical and Mechanical Properties of Mortar. *Journal of Minerals and Materials Characterization and Engineering*, **9**, 480-498.
https://doi.org/10.4236/jmmce.2021.95032

Received: July 28, 2021
Accepted: September 3, 2021
Published: September 6, 2021

Abstract

The mechanical and physical properties of TUFF from Korsimoro (Burkina Faso) were investigated for use as admixtures in clinker to make pozzolanic cement. Six different cement mortar specimens were prepared by replacing clinker with TUFF in ratios of 0%, 5%, 8%, 10%, 13% and 15% by mass. The flexural and compressive strengths of the specimens were determined at the ages of 2, 7, 28 and 60 days. The effects of the TUFF replacement ratio on workability, setting time and volume expansion were also examined. Based on the results, it was concluded that Korsimoro TUFF has pozzolanic activity and is suitable for use as an alternative adherent material in the cement industry.

Keywords

Pozzolan, Tuff, Admixture, Cement, Mortar

1. Introduction

In Burkina Faso, there is a large program of building housing, structuring buildings such as hospitals, administration and universities, road works and many other construction areas. The implementation of this major infrastructure program goes with high consumption of basic materials including cement which is one of the most used basic materials. It is in demand in virtually all areas of construction. Obtained from the clinker, which itself obtained by cooking clay ma-

terial and calcite at 1450˚C, cement is an energy-intensive compound [1]. In addition, its production is polluting because one ton of cement produced is equivalent to one ton of carbon dioxide released into the atmosphere. Cement industries were the world's leading air polluters. It is then necessary, even imperative, to find ecological materials that can at best partially replace cement. The high costs and negative environmental effects of frequently used cement materials have motivated research into alternative cementitious materials such as pozzolans [2] [3] and investigation of the pozzolanic properties of volcanic tuffs from the large volcanic deposits is therefore beneficial for the cement industry.

Pozzolanic materials are serious candidates. Among these pozzolanic materials, natural tuffs have been studied in some countries to better understand their pozzolanic reactivity. The use of pozzolans improves the mechanical holding of products by increasing C-S-H hydrates, reducing porosity due to their filler properties and reducing alkali-silica reactions [4]. This work mainly concerns the study of the physical-chemical characteristics, the thermal, mechanical and pozzolanic behavior of a raw material (Tuff). This study assesses the potential for the use of local raw materials from Burkina Faso as a pozzolan in cement. At clinker, we will bring quantities of tuff to obtain the best cement formula adapted to our sub-Saharan context. These will be Portland-type types of cement. The Portland cements composed result from the mixture of clinker in quantities at least equal to 65% and other constituents such as blast furnace dairy, fly ash, pozzolans, silica smoke, the total of which does not exceed 35%. Chemical properties, which are an important factor in the resistance of concretes to aggressive environments, concern the sulphuric anhydride (SO_3) content of less than 4% (4.5% for classes 42.5 R and 52.5) and chloride ions below 0.10%.

With this background, the study reported in this paper aimed to evaluate volcanic tuff from the central Anatolian province for its suitability for use in the cement industry.

For this purpose, standard test specimens were prepared by using volcanic tuff as a partial replacement of cement in concrete.

The specimens were mechanically and chemically tested to determine the pozzolanic properties of the volcanic tuff.

The properties examined include setting time, volume expansion and the flexural and compressive strength of cement mixtures. To eliminate the impact of the water/cement (w/c) ratio on the results, a constant ratio was used.

2. Materials and Methods

2.1. Materials

The samples studied in this work come from different localities.

The used clinker comes from the Cement Plant of the Heidelberg Group, where most of Burkina Faso's cement industries source.

Two other mineral raw materials used by some cement companies in Burkina Faso are classified as gypsum and tuff and will be named GYP and TUFF respec-

tively in the context of this work. GYP is a commercial material imported from Spain and TUFF comes from the central region of Burkina Faso specifically Korsimoro about 70 kilometers from Ouagadougou.

The sand used in all mixtures of formulated foamed concrete is standardized.

Each raw material was crushed and grounded. The fine powders were then mixed according to the designed proportions.

Figure 1 shows photo images of the raw materials used (clinker, GYP and TUFF).

Making and formulating mortar test tubes: first, the formulated cement ground to 80 μm and water (225 g) is introduced into a mixing machine to be mixed for one minute at a speed of 140 revolutions per min. After that, the sand (1350 g) is added and the mixture is then mixed again for 3 minutes at a speed of 280 revolutions per min. The mixture is introduced into 4 × 4 × 160 cm^3 prismatic molds and mechanically compacted using a shock wave apparatus. The molds containing the samples are covered with plastic film and stored in cold storage with a temperature of 20˚C ± 1˚C. Demolding is carried out after 24 hours and the specimens are stored in the laboratory at 20˚C ± 1˚C in a vessel containing water until the day of the test set at 28 days [5]. Table 1 shows the cement formulated composition used of the various mortars produced.

2.2. Methods

2.2.1. Pozzolanic Activity

The pozzolanic activity of a sample is related to its speed of lime fixation, the amount of lime it can fix for a given time and the nature of the new phases. These different factors influence the mechanical performance of the products

Figure 1. Raw materials.

Table 1. Cement formulated composition of test powders for mortars.

Composition of powders	Reference
95% Clinker + 5% GYP and 0% TUFF	C0
90% Clinker + 5% GYP + 5% TUFF	C5
87% Clinker + 5% GYP + 8% TUFF	C8
85% Clinker + 5% GYP + 10% TUFF	C10
82% Clinker + 5% GYP + 13% TUFF	C13
80% Clinker + 5% GYP + 15% TUFF	C15

that will be produced there. It is then necessary to combine several methods to better understand this pozzolanic activity. To this end, we combined chemical, mineralogical and mechanical methods.

The Frattini test and the saturated lime test are the two chemicals methods used to determine the pozzolanic activity of materials. These tests are based on the amount of free calcium hydroxide ($Ca(OH)_2$) removed after the hydration of silicates in pozzolans. It is known that calcium hydroxide is released during the hydration of C_3S and C_2S, which are the main components of a cement. When pozzolanic material is added to cement, the free calcium hydroxide and active silica can combine to form silicate hydrates, which are not soluble in water. This reduces the free calcium hydroxide in the system and this reduction shows that the added tuff has pozzolanic activity [6].

The Frattini test procedure consists of preparing a mixture of 20 g, consisting of 80% artificial portland cement with 20% of RHA added to 100 mL of distilled water. The mixture is kept at a temperature of 40˚C for eight days in hermetically sealed plastic boxes. After these eight days, the mixture is filtered through a pore-size filter paper. The hydroxide ions (OH^-) contained in the filtrate are then dosed with a dilute hydrochloric acid solution at 0.1 $mol{\cdot}L^{-1}$ using methyl orange as a color indicator. Then the calcium ions (Ca^{2+}) will be as well-dosed by an Ethylenediaminetetraacetate (EDTA) solution at 0.03 $mol{\cdot}L^{-1}$ using Patton and Reeders as a color indicator. The results obtained are illustrated by a graph giving the Ca^{2+} ions concentration expressed in $mmol{\cdot}L^{-1}$, which is equivalent to the amount of CaO according to the concentration of OH^- ion also expressed in $mmol{\cdot}L^{-1}$ [7].

The saturated lime test consists of preparing a mixture consisting of 1 g of TUFF and 75 mL of saturated lime solution initially prepared by dissolving 2 g of hydrated lime in 1 L of distilled water. The sealed mixture is kept during the test period set at 1, 3, and 7 days. The test is carried out from 10 mL of the filtered mixture. The OH^- and Ca^{2+} ions are respectively dosed with dilute hydrochloric acid solution and EDTA using the same procedure as in the Frattini test. Thus, from the quantity of calcium ions contained in the initial mixture, the amount of CaO fixed by the material is determined. After the Frattini test, the residues obtained were finely ground and then subjected to analysis. Qualitatively, thermogravimetric analysis (DTA/TG) was used to monitor not only the evolution of pozzolanic reactivity but also to identify the products resulting from pozzolanic reactivity.

For the mechanical method, the pozzolanic index was calculated. Prismatic mortars ($4 \times 4 \times 16$ cm^3) are made according to the TS EN 196-1 [7] standard. Several mortars with partial cement replacement (25% mass) are developed and stored at 20˚C in water before undergoing mechanical compression tests for 28 days. The pozzolanic index corresponds to the ratio of compression resistance of the mortar containing the pozzolan to the resistance of the mortar without pozzolan.

Quantification of the amorphous phase of the pozzolan is carried out by selective dissolution of silico-aluminous amorphous into diluted hydrofluoric acid at 1%.

The dry residues obtained indicate the level of amorphous in the material by Equation (1):

$$\%\text{amorphous} = \frac{m_{\text{sample}} - m_{\text{Residue}}}{m_{\text{sample}}} \quad (1)$$

where m_{sample}: sample mass; m_{residue}: mass of crystallized product obtained.

This method quantifies the soluble phase, which is considered potentially reactive; by difference assesses the solubilized fraction [8] [9].

The kinetics of the dissolution of the phases depend on their crystallinity, the fineness of the frame and their stability in acidic environments. The rate at which amorphous silico-aluminate compounds dissolve is faster than that of the crystalline phases.

2.2.2. Characterization Methods

The chemical analysis of the cement was carried out by X-Ray Fluorescence (XRF) and the sand has done in a previous study [10] by ICP-AES (Inducted Coupled Plasma-Atomic Emission Spectrometry). Mineralogical compositions were obtained by X-ray diffraction using Brüker D5000 type diffractometer with graphite rear monochromator, operating at 40 kV - 50 mA with Cu Kα_1 radiation. The machine was driven by Diffracplus D software version 2.2. The acquisition time was 60 min.

The water absorption (E) of the firing test pieces was determined according to ISO 10545-3 [11]. A mass m_1 of each specimen (dried at 105˚C in the oven) is immersed in boiling water for 2 h. After 4 h of cooling, the new mass m_2 of the wet specimen is weighed (±0.001 g precision). The difference in mass gives the mass of water absorbed by the specimen during this time. The open or apparent porosity P is deduced from the absorption of water and by exploiting its volume V.

The water absorption is evaluated according to Equation (2) and the open porosity is calculated using Equation (3):

$$E(\%) = \frac{m_2 - m_1}{m_1} \times 100 \quad (2)$$

$$P(\%) = \frac{m_2 - m_1}{V} \times 100 \quad (3)$$

Flexural mechanical properties are obtained by three-point flexural tests with prismatic specimens (4 × 4 × 16 cm^3). They were placed on two parallel supporting pins and the loading force is applied in the middle using a loading pin. The supporting and loading pins are mounted in a way to allow their free rotation about the axis parallel to the pin axis. This configuration provides uniform loading of the specimen and prevents friction between the specimen and the supporting pins [12]. The flexural strength is carried out with a hydraulic press

equipped with a 200 kN load cell at a controlled displacement rate of 0.5 mm/min. Equation (4) makes it possible to determine the limit stress in flexural strength [13].

Simple compression on the two half-pieces obtained after a rupture in bending using TONI TECNIK brand devices.

$$\sigma = \frac{3FE}{2le^2} \tag{4}$$

F is the intensity of applied force, E is the distance between the two supports of test specimens, l is the width of the test specimens, e is its thickness and σ is the breaking stress.

In order to determine the compressive strength, the half-prism resulting from the flexural strength is subjected to a monotonously increasing load until breaking.

Thus, the compressive strength is the ratio of the breaking load to the cross-section of the specimen. The value of the resistance R_C is obtained from Equation (5).

$$R_C\left(\text{MPa}\right) = \frac{P}{S} \tag{5}$$

With: S: average value of the section express in cm^2 and P the load express in KN.

The flexural and compression strength tests are carried out following standard TS EN 196-5 [14].

The mineralogical analysis obtained by the XRD made it possible to have an idea of the mineral phases in these foamed concretes.

The thermal analyses have been recorded for both Differential Thermal Analysis (DTA) and Thermogravimetry (TG). It was obtained with a SETARAM Setsys 24 using Pt crucibles, and a heating rate of 10˚C/min. Experiments were carried out with 50 mg of powder into the crucible and a pure α alumina calcined powder at 1500˚C serves as reference material in adequate quantity to reduce the calorimeter imbalance. The kiln atmosphere was air at atmospheric pressure.

3. Results and Discussion

3.1. Physical-Chemical Properties of Raw Materials

3.1.1. Basic Chemical Analysis and Fire Loss at 1000˚C

The chemical properties of the studied Clinker, TUFF and GYP are presented in **Table 2**. The chemical requirements of the Turkish standard TS 25 and ASTM C 618 [15] [16] are also listed in **Table 2**.

The chemical composition of the clinker conforms to the standard according to which: $SO_3 < 3\%$; $MgO < 4\%$; $Na_2O < 0.5\%$ and $K_2O < 1\%$ but the CaO/SiO_2 ratio = 3.13 is greater than 2 required by the NF EN 196-2 [17]. The loss on ignition of the clinker is 1.61%; this low value reflects its good quality and indicates the absence of untransformed clay phases (clay, limestone). This clinker can

Table 2. Chemical composition of raw materials: Mass %.

Samples	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	LOI*	Total
Clinker	20.8	5.4	4	65.2	1.6	1.1	0.24	0.7	1.6	100.64
TUFF	63.9	15	5	5.4	2.9	-	1.6	1	8.5	103.3
TS 25 (ASTM C 618)	>70 (>70)			-	<5	<3 (<4)	-	-	< 10	-
GYP	9.17	4.06	1.15	30.47	1.02	41.66	0.34	0.27	12.5	100.64

*Loss on ignition.

then be used in the formulations of our cement. The significant percentages of lime and silica can give the developed cement the required performance.

Chemical analysis indicated that the TUFF is principally composed of silica (approximately 64%), with calcium oxide, alumina and iron oxide with a total ratio of 25.36% and an alkali content of 2.55% (sodium oxide and potassium oxide). Silica, alumina and iron oxide have a total ratio of 83.9% that is superior to 70% as required by Turkish standard TS 25 and ASTM C 618 [15] [16].

The chemical composition of GYP shows that in addition to being a sulfo-calcium, it would contain alumino-silicates with a SiO_2/Al_2O_3 ratio = 2.26. It also contains iron or iron oxides or hydroxide. The loss on ignition of the GYP and TUFF, respectively 12.5% and 10.5%, are quite high and reflect a predominance of clay minerals in these samples [9]. They reflect a loss of water or impurities such as organic matter, carbonates etc.

3.1.2. Mineralogical Characterization of Raw Materials

Figures 2-4 show us the diffractograms of Clinker, TUFF and GYP respectively. The analysis of the X-ray diffraction spectra was carried out using the ASTM files.

The Clinker diffractogram (**Figure 2**) identified major minerals such as Calcium Silicate (Ca_3SiO_5), Larnite (Ca_2SiO_4); Calcium Aluminum Oxide ($Ca_3Al_2O_6$); Brownmillerite ($Ca_2(Al, Fe^{III})_2O_5$). It is these phases which are the basis of the setting and hardening phenomena of mortars and concretes through their reactions with water.

The main mineral phases identified in TUFF (**Figure 3**) are kaolinite, albite, dolomite, Calcium Aluminum Silicon Oxide Hydroxide, quartz and illite.

The diffractogram of the GYP (**Figure 4**) reveals the presence of gypsum ($CaSO_4{\cdot}2H_2O$), Hematite; Calcium Oxide Phosphate and quartz. The identification of gypsum suggests that this clay could be used as a regulator in cement.

The quantitative mineralogical balance of GYP and TUFF is carried out based on simplified chemical formulas expressed as oxides of the identified minerals. The results obtained are shown in **Table 3**.

3.1.3. Differential Thermal Analysis (DTA) and Thermogravimetry (TG)

The differential thermal analysis and thermogravimetric (DTA/TG) curves of TUFF and GYP are shown in **Figure 5** and **Figure 6**, respectively. In the case of

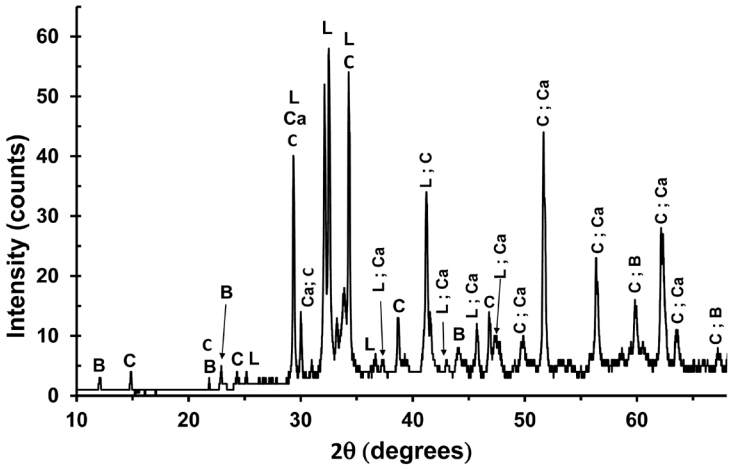

Figure 2. Diffractogram of Clinker. C: Calcium Silicate (Ca_3SiO_5); L: Larnite (Ca_2SiO_4); Ca: Calcium Aluminum Oxide ($Ca_3Al_2O_6$); B: Brownmillerite ($Ca_2(Al,Fe)_2O_5$).

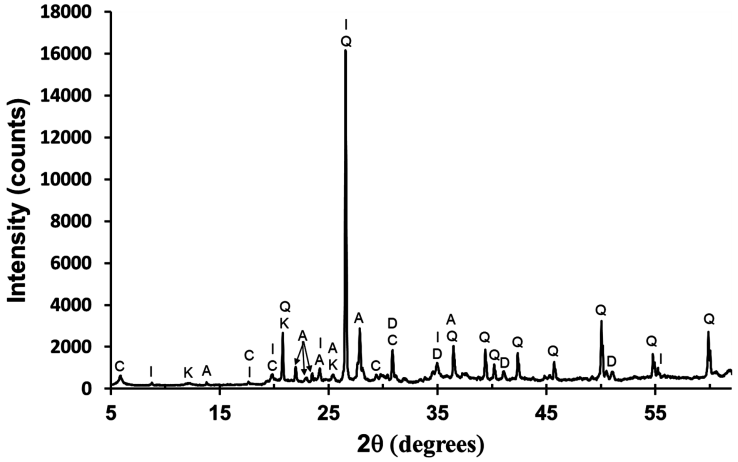

Figure 3. Diffractogram of TUFF. A: Albite ($Na_{0.98}Ca_{0.02}Al_{1.02}Si_{2.98}O_8$); C: Calcium Aluminum Silicon Oxide Hydroxide ($Ca_{0.5}(Al_2Si_4O_{11}(OH))$); K: Kaolinite ($Al_2Si_2O_5(OH)_4$); I: Illite ($K_{0.78}Mg_{0.18}Ti_{0.01}Al_{2.46}Si_{3.36}O_{10}(OH)_2$); Q: Quartz ($SiO_2$); D: Dolomite ($CaMg(CO_3)_2$).

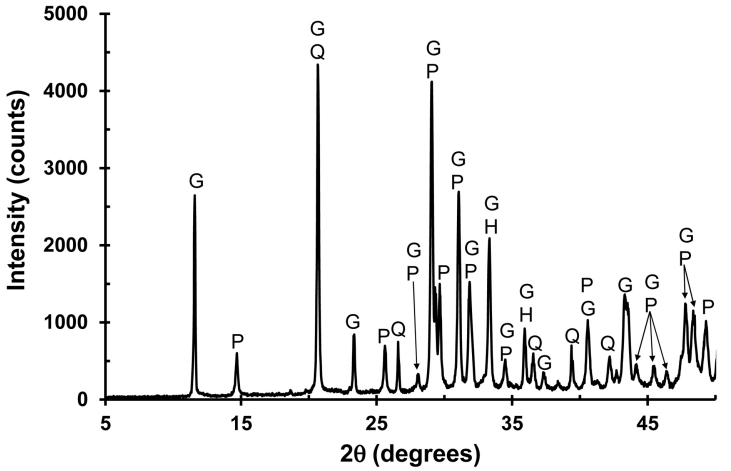

Figure 4. Diffractogram of GYP. H: Hematite (Fe_2O_3); Q: Quartz (SiO_2); P: Calcium Oxide Phosphate ($Ca_4O(PO_4)_2$); G: Gypsum ($Ca(SO_4)(H_2O)_2$).

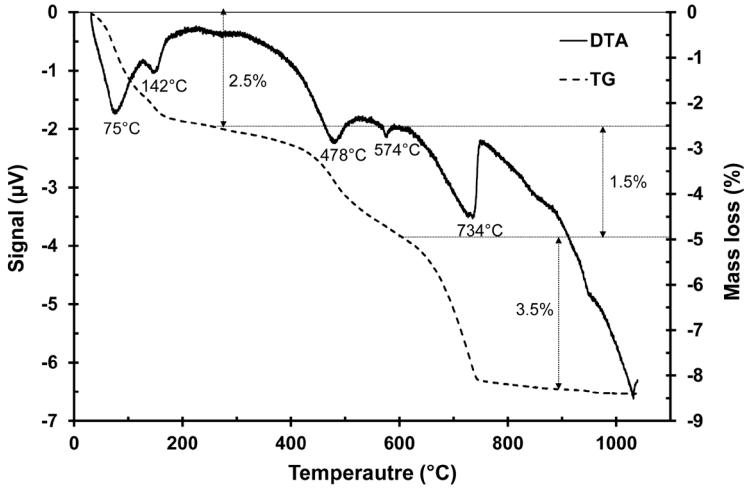

Figure 5. DTA/TG thermograms of TUFF.

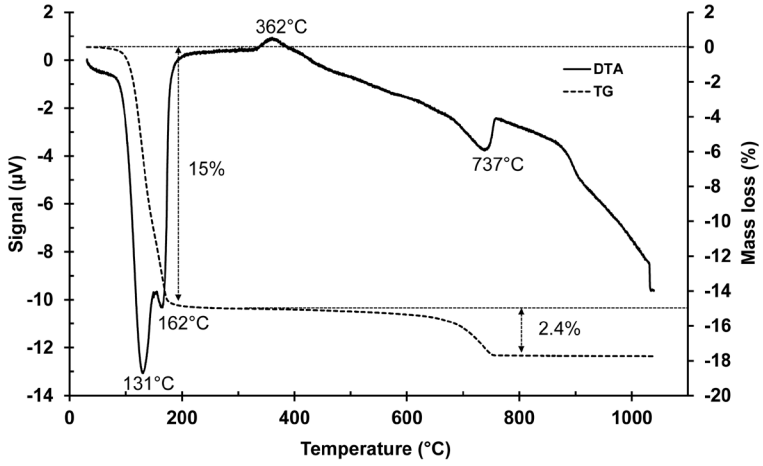

Figure 6. DTA/TG thermograms of GYP.

Table 3. Mineralogical composition of TUFF and GYP (mass %).

Minerals	Kaolinite	Illite	Quartz	Albite	Dolomite	ASH*	Gypsum	COP**	Hematite	Total
TUFF	8	11	32	13	12	21	-	-	-	97
GYP	-	-	7	-	-	-	61	27	1	96

*Calcium Aluminum Silicon Oxide Hydroxide, **Calcium Oxide Phosphate.

TUFF, we distinguish five characteristic endothermic peaks. A first endothermic peak at low temperature centered at 70˚C corresponds to the start of weakly bound water (hydration water). A second endothermic peak at 140˚C would correspond to the decomposition of hydroxides of hydrates of aluminum and calcium silicate. These two phenomena are associated with 2.5% of mass loss. The third endothermic peak centered at 472˚C which reflects the dehydroxylation of clay minerals such as kaolinite and illite. The corresponding mass loss is 1.8%. An endothermic hook at 573˚C corresponds to the transformation of α-quartz into β-quartz. Finally, the peak at 735˚C which is associated with 3.7% mass loss, corresponds

to the decarbonization of dolomite (decomposition of residual calcite). The exothermic peak which should illustrate the phenomenon of the reorganization of meta-kaolinite is less appreciable either because of the endothermic phenomenon of the decarbonization of dolomite which covers part of its temperature range, or the low kaolinite content of this material. Another exothermic peak, located at 735˚C, corresponds to the structural reorganization of the metakaolin-dolomite mixture and the recrystallization of new phases [6] [18] [19].

The plot of the differential thermal analysis curve for GYP (**Figure 6**) indicates the existence of a first endothermic phenomenon centered at 130˚C corresponding to the transformation of calcium sulfate dihydrate into hemihydrate according to the process (Equation (6)):

$$CaSO_4 \cdot 2H_2O \rightarrow CaSO_4 \cdot 1/2\,H_2O + 3/2\,H_2O \quad (6)$$

The hemihydrate formed is decomposed in turn from about 163˚C into soluble anhydrite according to the reaction (Equation (7)):

$$CaSO_4 \cdot 1/2\,H_2O \rightarrow CaSO_4 + 1/2\,H_2O \quad (7)$$

These two reactions (Equations (6) and (7)) are accompanied by a mass loss of 15% observable on the ATG thermogram. An exothermic effect is then recorded between 300˚C and 400˚C, reflecting the crystallographic transition from soluble anhydrite, or anhydrite III to anhydrite II [20]. Another endothermic peak at 739˚C corresponds to the decomposition of tetra-calcium phosphate associated with gypsum. According to Hafd Dehbi [21], tricalcium phosphate loses after heating to 700˚C one molecule of water for every six molecules of tricalcium phosphate. The chemical formula for hydrated trica1cium phosphate is written $(Ca_3(PO_4)_2)$ 1/6 H_2O. The dehydration of the trica1cium phosphate occurs without change of structure up to 700˚C and in an irreversible manner. Above 700˚C, it changes its structure by transforming into trica1cium phosphate γ [21].

3.1.4. Evaluation of Pozzolanic Activity

The pozzolanic activity of a material can be assessed based on its chemical composition and its content of glassy phases.

According to TS 25 and ASTM C618 [15] [16] standards for pozzolanic material, a natural pozzolan must contain a minimum of 70% SiO_2 + Al_2O_3 + Fe_2O_3. The results of the chemical analysis (**Table 2**) show that THE TUFF meets these standards. Indeed, the sum of the percentages of major oxides % SiO_2 + % Al_2O_3 + % Fe_2O_3 is 83.9%. Tuff could therefore be a good pozzolana. A relatively high rate of active phases (SiO_2 + Al_2O_3) with 78.9% could indicate the acid character of this material [22].

The amount of the amorphous phase of the tuff was evaluated by selective diffusion in hydrofluoric acid. The rate of amorphization of our materials used can influence their reactivity to the pozzolanic reaction. In fact, this level of amorphous phase corresponds to the proportion of materials that will be able to react easily, at room temperature and in the presence of water with calcium hydroxide. According to this method, the quantification of the amorphous phase

contained in the pozzolan (TUFF) is 40%. This amorphous phase in this material is responsible for its pozzolanicity. This amorphous phase content is comparable to that identified by Pichon and Segui [9] [23] in a pozzolana extracted from the quarry at the Volvic station (35%).

Figure 7 shows the consumption of CaO by the tuff. TUFF powder is dissolved in a saturated lime solution. The amount of lime fixed by the pozzolan is determined by measuring the concentration of dissolved residual calcium. According to the results of Figure 7, the consumption of lime is low at a young age (1 to 3 days). Between the 3rd and the 7th day the consumption is very high, on the other hand, it becomes slow between the 7th and the 28th day.

The results of the Fratini test are shown in Figure 8. The amount of lime fixed by the sample (TUFF) is located below the portlandite solubility curve [13] [24]. This result then confirms the appreciable pozzolanic reactivity of the tuff. These results also corroborate those obtained by the lime saturation method.

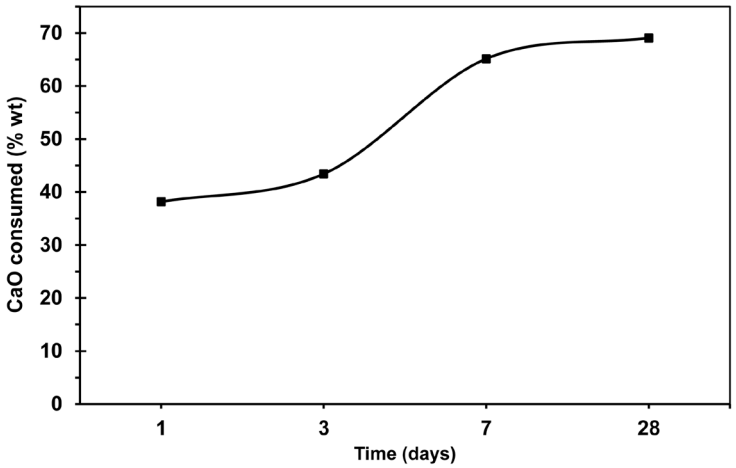

Figure 7. Lime saturation of TUFF.

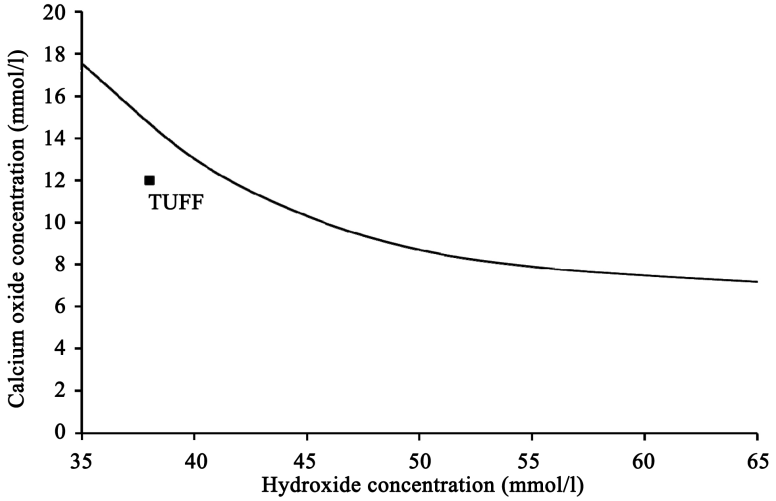

Figure 8. Calcium oxide—hydroxide solubility relationship of volcanic tuff according to standard values of TS EN 196-5 [14].

3.2. Formulation and Characterization of Pozzolanic Cements

3.2.1. Chemical Characteristics

The chemical composition of the various cement formulated as well as that of the control cement (C0) are determined according to standard using X-ray fluorescence. The results obtained are reported in Table 4.

The results of chemical analyzes follow the logic of dilution by tuff. Silica, abundant in TUFF, increases when we go from C0 to C15, on the other hand, lime evolves in the opposite direction. In addition, the sum of the oxides % CaO + % SiO_2 is greater than 50%, the minimum value required by standard NF EN 197-1 [25].

3.2.2. Ratio Water/Cement (W/C) and Setting Time

The W/C ratio which determines the quantity of water necessary for mixing the cement decreases as the rate of addition of tuff increases from 0% to 15%. This would reflect the fact that the addition of pozzolan reduces the amount of mixing water (Table 5). Furthermore, the low W/C ratio is advantageous because it allows better workability of fresh concrete.

C0, C5, C8, C10, C13 and C15 cements have an initial set of over 60 min, so they comply with standard TS EN 196-3 [26]. The initial and final settings of C5, C10 and C15 are delayed relative to CPA (C0). It reaches its maximum from C10, *i.e.* 10% TUFF (Table 5). The addition of TUFF extends the setting time up to 10% and beyond (15%) this rate improves it. Indeed, a long setting time promotes the workability of fresh concrete and maneuver time. These delays in setting times could be due to the decrease in the speed of the hydration process: part of the quantity of water necessary for the hardening of the cement alone is consumed by the pozzolan or to the dilution effect of the grains of cement. The amount of portlandite released by the hydrated cement and necessary for the pozzolanic reaction could be insufficient.

Table 4. Chemical characterization of tuff-based cements.

Samples	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	LOI*
C_0	19.94	5.34	3.44	61.38	1.56	2.92	0.2288	0.661	2.44
C_5	22.3	5.83	3.59	58.24	1.65	3.02	0.2964	0.688	2.9
C_{10}	23.78	6.42	3.75	54.83	1.78	3.06	0.3633	0.717	3.1
C_{15}	25.79	6.84	3.71	53.05	1.8	2.56	0.3381	0.48	3.11

Table 5. Setting times and volume expansion.

Series	Water/Cement ratio	Setting time: min	
		Initial	Final
C_0	24.4	191	297
C_5	23.2	202	279
C_{10}	22.8	227	363
C_{15}	22	202	300

3.2.3. DTA/TG of Formulated Cement Specimens

In order to understand the thermal behavior of the mortars at 28 days and also to appreciate the phases not identifiable with the DRX, we recorded the DTA/TG curves of the mortars at 28 days. The thermograms are given in Figure 9. The DTA curves mainly indicate three endothermic peaks and a hook. The first broad endothermic peak which appears to be double between 30˚C and 192˚C corresponds to the departure of water from the C-S-H hydrates in each of the samples. It is more pronounced for C0. It is associated with a mass loss of 1.5% for C5, 1.8% for C10 and 2.5% for C0. These mass losses are relatively low. The second peak between 400˚C - 460˚C corresponding to the dehydration of portlandite ($Ca(OH)_2$), this peak is associated with a mass loss of 0.9% for C5, 1.2% for C10 and 1, 8% for C0. The third peak between 810˚C and 890˚C corresponds to the transformation of calcite into lime with the release of CO_2. It is associated with a mass loss of 0.8% for C5, 1% for C10 and 1% for C0. The DTA/TG curves of the different formulated cements make it possible to identify the main hydrates formed through their loss of mass (CSH, CH, C) [22]. The DTA/TG curves also make it possible to draw the following conclusion: the pozzolanic reaction during which there is the formation of HSC to the detriment of CH has taken place.

3.3. Characterization of Pozzolanic Cement Mortar

3.3.1. Mechanical Properties of Cement

The compressive strength, as well as the flexural strength of cement mortars, are done on test specimens illustrated at Figure 10.

The evolution of the mechanical behavior is followed as a function of the storage time. The compliance of a batch of cement is assessed with regard to the compressive strength [13].

Figure 11 shows the effect of TUFF on the flexural strength of mortars. All values of flexural strength at different ages are following CEM IV cement standards. We notice that the resistances increase with time for all the mortars.

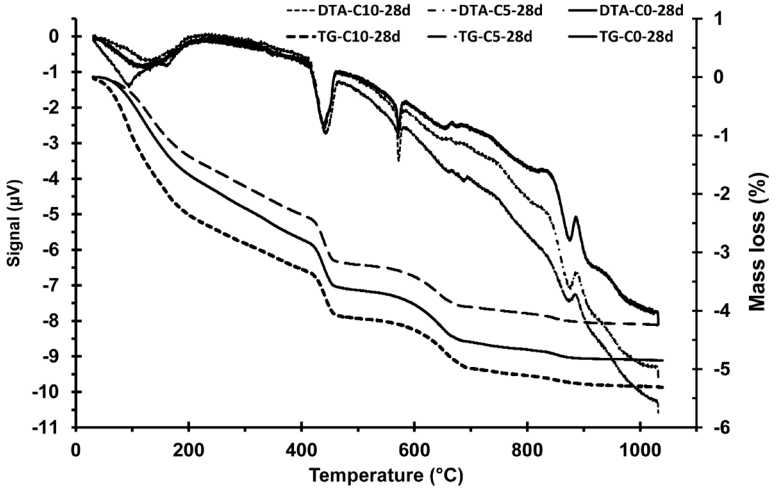

Figure 9. DTA/TG thermograms of mortars at 28 days of formulated cements.

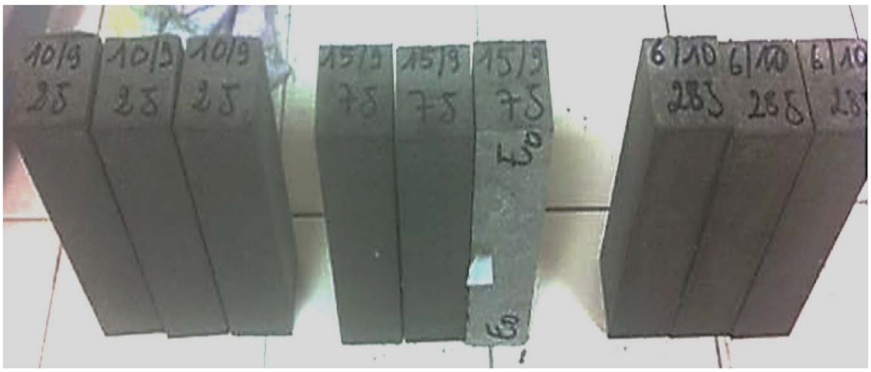

Figure 10. Image of some mortar specimens.

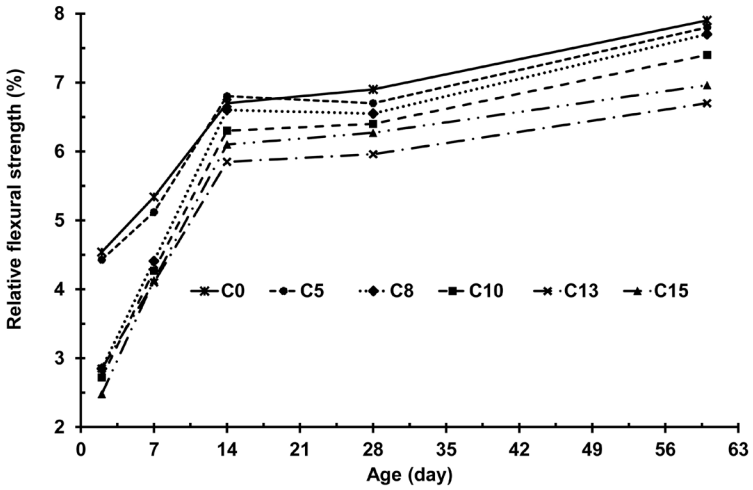

Figure 11. Variation of flexural strength of mortars with respect to time and replacement ratio.

Those of mortars with the addition of pozzolan (TUFF) grow in the long term. The increase in these flexural strengths for mortars with tuff is slow.

Figure 12 shows the effect of TUFF on the compressive strength of mortars. All values of the compressive strength at different ages are in accordance with the standards on CEM IV cement. Compressive strength test for specimens can be seen from their results that, whatever the type of mortar, the compressive strength changes positively with age.

The results of our study show the interest of using pozzolan as a partial replacement for cement on the mechanical performance of mortars. Cement-based mortars with the addition of natural pozzolan (TUFF) have increasing mechanical resistance. However, values remain below mortar without adding C0. Pozzolan increases mechanical resistance thanks to its reactivity with the lime released by the hydration of the cement. At any age, the resistance of the different mortars is inversely proportional to the quantity of pozzolan substituted. The strength of the C8 cement-based mortar develops interesting and increasing strengths that can probably exceed that of the C0 reference mortar in the long term, due to the slow pozzolanic reaction which could be triggered late by

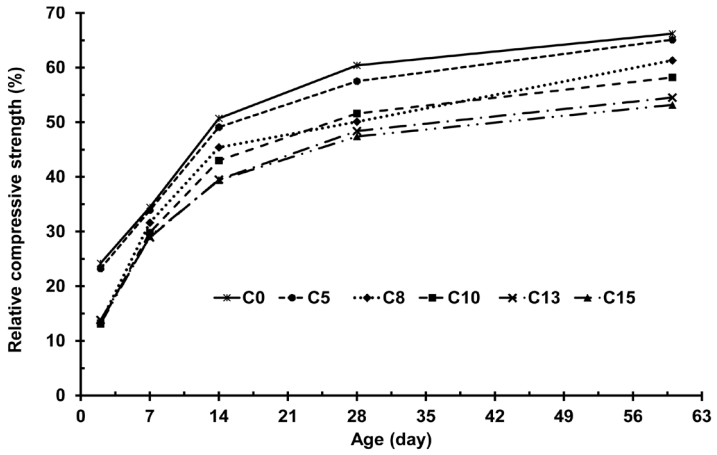

Figure 12. Variation of compressive strength of mortars concerning time and replacement ratio.

improving the mechanical compression performance. These results show that over time, and during the first 60 days, there is a slight increase in the resistance of all shades. From 28 days, the resistances of the C0 shade grow slowly compared to the others. Beyond 28 days, the progression of resistance is more pronounced.

A similar study with the addition of pozzolan to concrete was performed by Seynou *et al.* [27] and similar results were obtained. In the work reported by H. Biricik and S. Karapınar [5], the fineness of the volcanic tuff was about 2.5 times higher than the fineness of the volcanic ash used by Hossain and Lachemi [28]. Therefore, the flexural and compressive strengths of specimens of series C8 (8% TUFF) were similar to those of the reference groups at the age of 28 and 60 days.

As a result of the mechanical tests, it can be concluded that the studied TUFF is pozzolanic in character and all replacement level used is a good ratio for the mortar mixtures investigated in this study.

The improvement in workability with the addition of TUFF may be ascribed to its high fineness and/or the spherical shape of its particles. The unit weight of the mortars decreased with increasing TUFF replacement. This is due to the effect of the lighter TUFF replacing the comparatively heavier cement [5].

3.3.2. X-Ray Powder Diffraction Analysis and SEM of Formulated Mortars

Figure 13 shows the diffractograms of the different mortars from the formulated cements. We have identified the main hydrates commonly found in mortars. However, we see a slight decrease in portlandite peaks with an increasing rate of tuff addition. This could be explained by its consumption over time through a pozzolanic reaction. On the other hand, other peaks grow (C_3AH_6 and CSH) in the diffractograms of the mortars with the addition of tuff. The phases corresponding to these peaks originate from the hydration of C_3S, C_2S, C_4AH and C_3A in the sample without tuff, but their growth in the other samples indicates the existence of another source. Thus, we can say that the additional effect of its hydrates comes from the reaction between the minerals of the tuff and the portlan-

dite. The calcite present comes from dolomite. It could also come from the carbonation reaction of lime in cement by carbon dioxide in the air.

Figure 14 shows SEM micrographs of the cement paste series containing C0, C5, C10 and C15 (respectively 0%, 5%, 10% and 15% TUFF at the age of 7 d. The ordinary Portland cement specimen (0% TUFF) showed a typical heterogeneous distribution of calcium silicate hydrate (C–S–H) and calcium hydroxide. Needle-like crystals (ettringite) were also observed. The existence of needle-hydrates was present in all cases and a denser microstructure was exhibited. The pozzolan reactivity increases the formation of hydrates CSH to the detriment of portlandite and thus increases the mechanical properties. Fine particles packing the space between the large particles and increase the specimen's density.

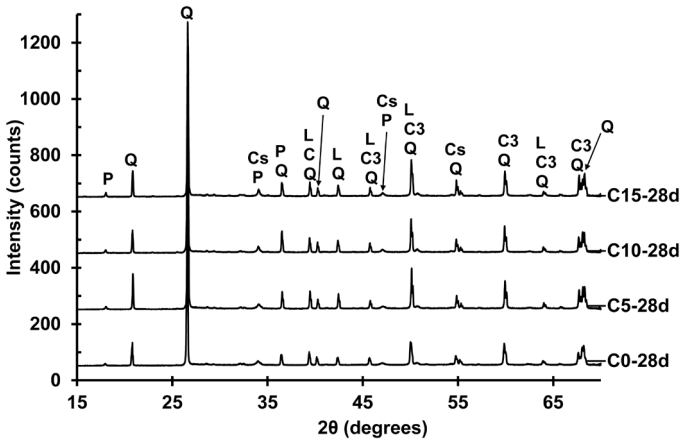

Figure 13. X-ray powder diffraction analysis of the different mortars at 28 days of the formulated cements Q: quartz (SiO_2); P: Portlandite ($Ca(OH)_2$); C3: Calcium Silicate (Ca_3SiO_5); Cs: Calcium Sulfate Sulfite ($Ca_3(SO_3)_{2.12}(SO_4)_{0.88}$); L: Larnite ($Ca_2SiO_4$); Calcite ($CaCO_3$).

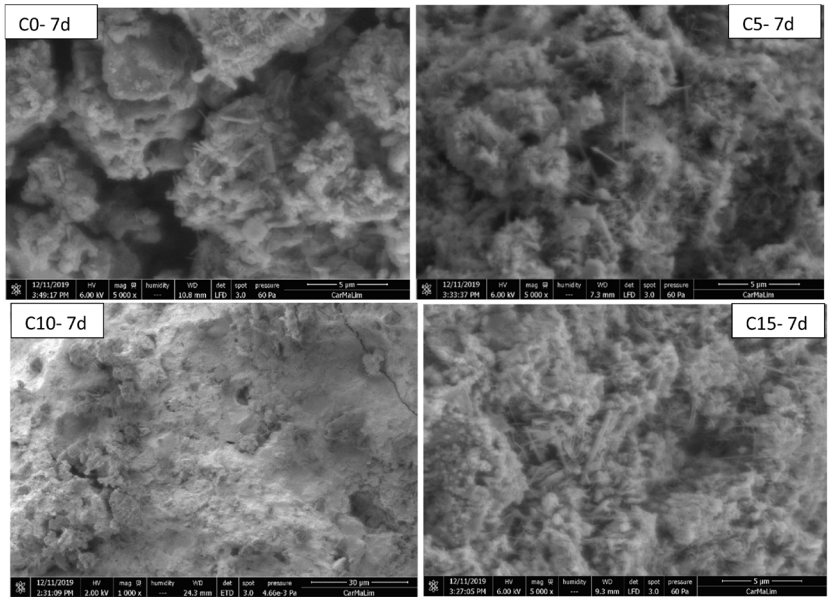

Figure 14. SEM images of mortar specimens after 7 d of curing.

4. Conclusion

Our work consisted, through the characterizations of the raw materials, in showing that the materials chosen for the study are suitable for the formulation of formulated cements that meet the standards in force on cement. The level of total silica (63.9%), of amorphous silica (40%) and the results of the Fratini test and the saturation test with lime confirmed the choice of this raw material as pozzolan. As for the other materials (clinker, and gypsum), which are part of the cement mix, we did the DRX, DTA/TG and the SEM to confirm the different expected phases. The results of these tests prove that it is a good clinker based on the French and Turkish standards which define its materials and gypsum which, however, is associated with other minerals. Six cements of various compositions were formulated (C0, C5, C8, C10, C13 and C15). We performed a chemical characterization (XRF) to verify their compliance with the standards which sets the minimum sum of the major oxides % CaO + % SiO_2 at 50%. From the results of the physical and mechanical tests, we can say that all four cements meet the requirements of standard NF EN 196-1. This standard states that the strength class of cement depends on its strength at 28 days. The four formulated cements have strength greater than 42.5 at 28 days. However, for C5 cement, the resistance at young age is greater than 20 MPa, C5 is qualified as R according to standard NF EN 196-1. In addition, through our natural pozzolan, we were able to show the possibility of substituting up to 15% clinker while respecting cement standards.

Conflicts of Interest

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

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