



Effect of temperature on pozzolanic reaction of Tunisian clays calcined in laboratory

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Abstract

The use of natural calcined clay as supplementary cementitious materials for the replacement of a portion of cement has become increasingly interesting. It is used for reducing the cement content in mortars and concrete production and also for improving strength and durability of concrete construction. In this context, the objective of this study was to make calcined clay in laboratory using two Tunisian clays burnt at 600, 700 and 800 °C and to study the effect of temperature on Pozzolanic reaction in terms of physical, mechanical and microstructure properties. Here, we studied the thermal and chemical properties, mechanical compressive strength of mortars, electrical conductivity as well as the physical properties, namely Blaine specific surface area, average particle diameter, pycnometer density, to evaluate its pozzolanic effect by substitutions of cement (5, 10, 15 and 20%). The results show the beneficial effect of adding calcined clay at different temperatures of calcinations on these properties. Besides, the average particle diameter increased with temperatures which agglomerate the particles. The Blaine specific surface area of calcined clay exceeded that of cement. Furthermore, the substitution of cement by calcined clay enhanced the compressive strength. All samples showed the development of strength between 28 and 90 days.

Keywords Calcined tunisian clays · Pozzolanic reaction · Physical properties · Microstructure · Mechanical properties

1 Introduction

The desire to improve the performance of cement-based materials has led to an increased use of pozzolanic materials which are siliceous or silico-aluminous materials having no binding properties. However, in the presence of water, they react chemically with calcium hydroxide (CH) to form binding compounds. Pozzolans are binding materials independently of the chemical and physical phenomena responsible for hardening [1–5].

Pozzolanic materials are divided into two types: natural and artificial materials. The latter, such as calcined clay, fly ash and slag, are produced by various heat treatments [6–9]. Calcined clays are considered as a pozzolanic

material due to their siliceous or siliceous aluminous nature. They are obtained by burning at a temperature that depends on the nature of the materials and the heating conditions [7, 10, 11].

Silica, alumina and iron oxide content along with temperature and calcination time have a significant effect on the physical properties of the clay [12]. A large demand for water has been noticed in mineral structures. To keep the same workability, we must add water that reduces the mechanical strength of the concrete and thus makes it difficult to distinguish the pozzolanic activity of the addition. Mortars containing some amounts of pozzolans are more viscous than those with no pozzolans addition. Hence, in

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order to obtain identical consistency, it is essential to use a super plasticizer [2, 13, 14].

Elinwa [15] determined the hydration time of cement by the addition of calcined clay using the Vicat apparatus. He showed that the hydration temperature decreases with the percentage of calcined clay added. Furthermore, he proved that the degree of hydration increases with the percentage of the addition during the first 24 h.

According to Chakchouk et al. [16], pozzolanic activity depends on several variables, namely the calcination temperature, the shape and size of particles as well as the calcination time.

The use of natural calcined clay as supplementary cementitious materials as a replacement of a portion of cement in concrete is becoming interesting. It is used not only to reducing the cement content in concrete production but also to improve strength and durability of structural concrete.

Addition of calcined clay plays an important role in the mechanical behavior of mortars and concrete. Al Rawes et al. [17] showed that there is no direct relationship between calcination time and compressive strength of mortar. However, Habert et al. [18] noted that the latter depends on the type of clay and the calcination temperature. Chakchouk et al. [16] showed that if the calcination temperature is higher than 700 °C, the strength increases with calcination time. However, Alkhatib et al. [19], has shown that the substitution of a proportion of 10 to 25% of the cement mass by calcined clay improves the compressive strength of mortars to reach 27% at 7 days, 32% at 28 days and 13% at 365 days.

Indeed, Sabir et al. [2] showed that Calcium Aluminates hydrates (CAH) and calcium silicate hydrate (CSH) increase with the increase in the addition percentage. They are responsible for increasing strength, which seems to depend on the mineral content [20] and which is enhanced by the chemical reaction of pozzolans with the calcium hydrate (CH) released during the process of cement hydration.

In addition, several authors have studied the influence of Metakaolin on the microstructure and properties of cement pastes and concrete. The additions reduce pores sizes and change their distribution [2, 3, 13]

Pozzolans lead to a closed porosity which improves the mechanical strength and durability due to the formation of a greater amount of CSH and also to the absence of

pore connection. Therefore, the incorporation of pozzolans into the cement allows a better hydration, a decrease in the number of pores and a reduction in the volume of the mix water [21].

Tunisia has large deposits of useful minerals that can be valuable for industrial operations in order to meet the important needs of the construction industry and public works. For this reason and for their wide availability in Tunisia as well as their physiochemical characteristics, they can be used to produce calcined clays. Therefore, the objective of this study was to develop Tunisian clay to make a calcined clay in laboratory and to study the effect of temperature on pozzolanic reaction. Calcined Tunisian clay's performance in terms of physical and mechanical properties as well as microstructure of mortars were studied.

2 Materials

2.1 Sand and cement

The sand (S) of 0/4 size had a density equal to 2.66 g/cm³ and a fineness modulus equal to 2.36. The cement used (C) was a Portland cement type CEM I 32.5 MPa. It had a specific gravity equal to 2950 kg/m³ and a Blaine surface area of 301.2 m²/kg. Its chemical composition is detailed in Table 1.

2.2 Crude clay

2.2.1 Geological presentation

The southern Atlas of Tunisia has large outcrops of clay formations that are very rich in Smectites, illites and kaolinites. The region covering the governorate of Gabes in the south of Tunisia is characterized by large outcrops of argillaceous nature (Fig. 1) [22]. Particular attention has been granted to the clay formations of ElHamma region. The study's first clay (clay 1), greenish in color, is located in JbelAidoudi. It is located about forty kilometers from the city of Gabes and is located in the far east of the northern chain of Chotts. JbelAidoudi's litho-stratigraphic section is composed from bottom to top by sands, dolomites and dolomitic limestones, slightly sandy limestone, gypsum green marl alternations, greenish veins with millimetric veins of gypsum and marly limestones. The second clay

Table 1 Chemical analysis of raw clays

	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	SO ₃	K ₂ O	MgO	Na ₂ O	Mn ₂ O ₃	P ₂ O ₅	TiO ₂	ZnO	PF
Clay 1	3.39	50.44	20.25	14.4	0.39	1.06	2.5	1.48	0.06	0.17	1.64	0.2	4.02
Clay 2	11.36	45.02	13.35	7.1	0.82	1.49	3.46	0.45	0.09	0.15	0.89	0.16	10.3
Cement (C)	62.15	16.51	3.59	2.62	3.59	0.5	1.05	0.09	-	-	-	-	0.96



Fig. 1 The clay rocks in the Governorate of Gabes [22]

(clay 2), red in color, is located in El EjjijElHamma. The clays of the Aleg formation of JebelAidoudi consist of alternating layers consisting of smectic red and green metric clays as well as few levels of carbonates and thinner gypsum [22]. The Aleg formation, east of the northern chain of Chotts at JbelAidoudi (El Hamma sheet) is formed of clay facies with a thickness of about 70 m surmounted by 50 m of green clays with fibrous gypsum seal [23]. The choice of clays is based on obtaining a better pozzolanic addition of a calcined natural clay.

2.2.2 Raw clay characterization

The samples taken from the two deposits were identified. As a result, mineralogical and chemical analyses as well as heat treatment were carried out.

2.2.3 Physical properties

Table 2 summarizes the determined physical properties of the two clays (clay 1 and clay 2), such as: the initial water

content (W_n), the liquid limit (W_L), the plasticity limit (W_p), the plasticity (I_p), consistency index (I_c) and density (ρ_{abs}) (NF P 94-051, NF P94-050). According to the plasticity diagram of Holtz and Kovacs, clay 1 can be classified as very plastic and clay 2 as plastic with a plasticity index equal to 50.4% and 38%, respectively. The laser particle size curve of the clays is given in Fig. 2 (NF P 18-560). Clay 1 is composed of 73% of silt and 27% of clay minerals, while clay 2 is composed of 72% of silt and 26% of clay minerals.

2.2.4 Chemical analysis

Table 1 summarizes the chemical composition corresponding to the two clays. The results of the chemical analysis show that their main constituents are silica (SiO_2), alumina (Al_2O_3) and iron oxides (FeO). Calcium oxide (CaO) is reported due to the abundance of carbonates, which are responsible for high fire losses. Potassium (K_2O) and sodium oxide (Na_2O) are attached to clay minerals and feldspars. The significant loss of clays is related to dehydroxylation of clay minerals [23]. It is observed that for

Table 2 Physical properties of raw clays

	W_n (%)	W_L (%)	W_p (%)	I_p (%)	I_c (%)	ρ_{abs} (g/m ³)
Clay 1	4.2	92.3	41.83	50.48	1.74	2.83
Clay 2	2.5	61	23	38	1.54	2.01

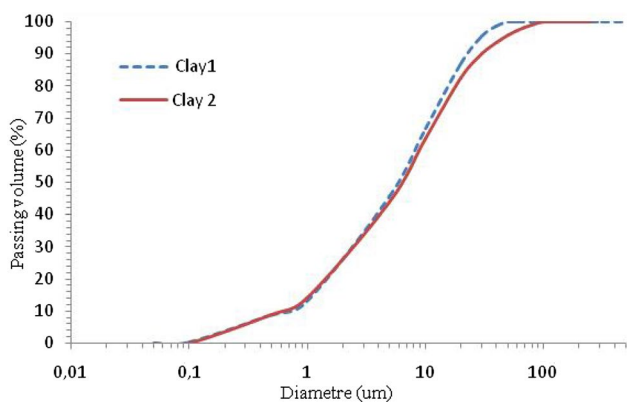


Fig. 2 Lazer particle size distribution curve (clay 1 and 2)

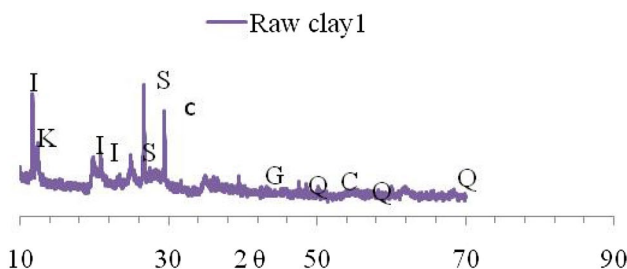
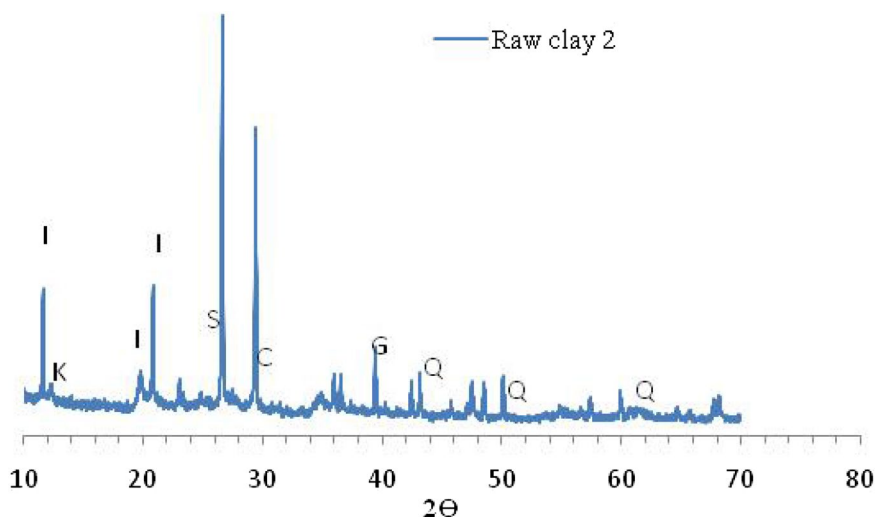


Fig. 3 Mineralogical composition of raw clay 1: I: Illite, K: Kaolinite, S: Smectite, G: Geothite, C: Calcite, Q: Quartz

clay 1, the silica content is less important (50.44%) compared with clay 2. Alumina is also of the order of 20.25% and 13.35% for clay 1 and 2, respectively. K_2O indicates the presence of illite in both clays. The Magnesium oxide (MgO) indicates the presence of smectite in greater proportion in the second clay. Clay 1 is rich in kaolinite and illite with a small amount of smectite compared to clay 2.

Fig. 4 Mineralogical composition of raw clay 2: I: Illite, K: Kaolinite, S: Smectite, G: Geothite, C: Calcite, Q: Quartz



2.2.5 Mineralogical analysis

Figures 3 and 4 show the X-ray diffraction test performed with $K\alpha_1$ radiation of copper. Among the clay minerals in raw clay 1 and clay 2 are smectite (S), illite (I), kaolinite (K), calcite (C) and Quartz (Q).

2.2.6 Thermal analysis

Thermal analysis [differential thermal analysis (DTA)/thermogravimetric analysis (TGA)] are determined simultaneously in a Setaram differential calorimeter device (SETSYS evolution) with argon shielding gas and Helium, an inert gas. A finely ground sample was introduced into an oven where the temperature was raised from room temperature to 1000 °C with a speed of 10 °C/min. The DTA/TGA curves shown in Figs. 5 and 6 depict three endothermic peaks.

- Endothermic peak at 100 °C for clay 1 and at 130 °C for clay 2. These peaks indicate the evaporation of absorbed moisture and interlayer water.
- Endothermic peaks around 470 °C (clay 1) and 460 °C (clay 2). These peaks indicate the de-hydroxylation of kaolinite with traces of illite as well as the formation of metakaolinite.
- Endothermic peak at 640 °C for clay 1 and at 680 °C for clay 2 corresponding to the transformation of quartz.

The loss of mass is equal to 17% for clay 1 and 15.9% for clay 2. Kaolinite is characterized by a significant loss of mass between 400 and 600 °C which corresponds to its de-hydroxylation. The amount of kaolinite can then be calculated from the amount of water released between

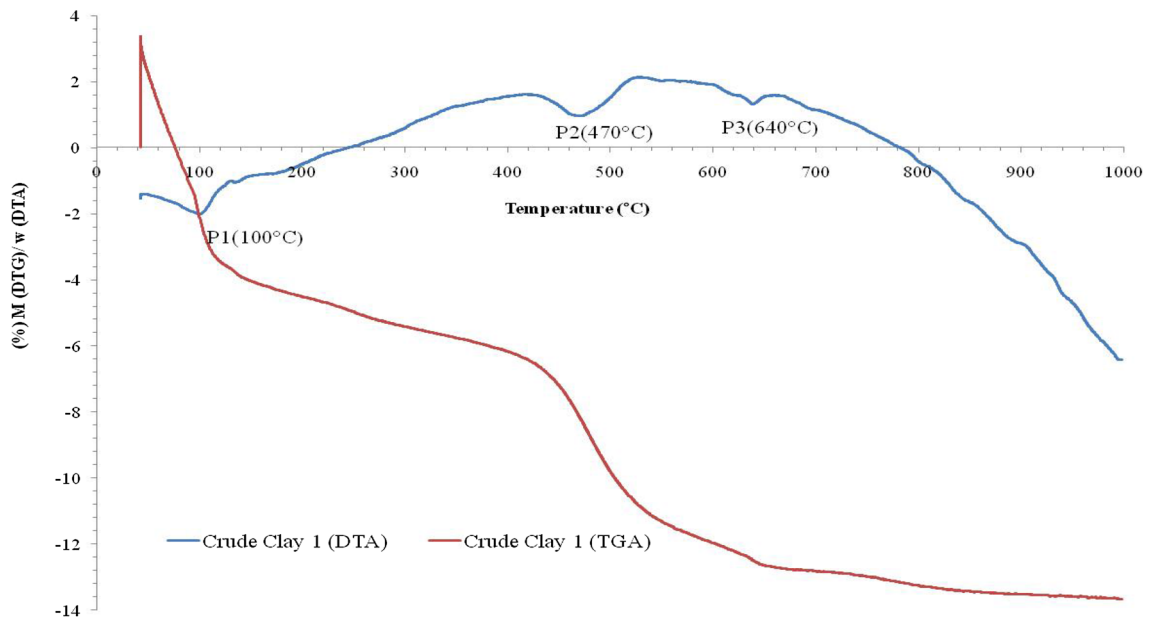


Fig. 5 DTA/TGA of raw clay 1

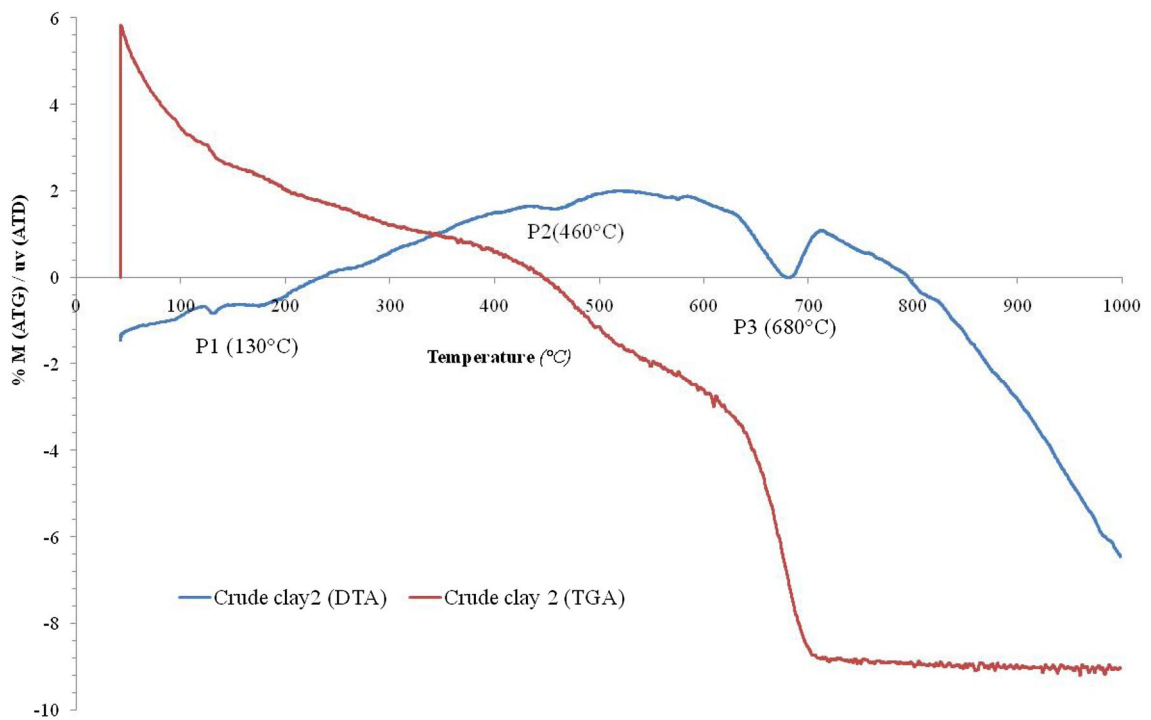


Fig. 6 DTA/TGA of raw clay 2

Table 3 Physical properties of calcined clays

Clay	Clay 1			Clay 2		
	600 °C	700 °C	800 °C	600 °C	700 °C	800 °C
Temperature	600 °C	700 °C	800 °C	600 °C	700 °C	800 °C
Calcination time	1 h	1 h	1 h	1 h	1 h	1 h
Density (g/cm ³)	2.48	2.44	2.35	2.6	2.3	2.4
The Blaine area (Kg/m ²)	457	420	307	475	424	525

Fig. 7 Effect of calcination temperature on the granulometry of clay 1

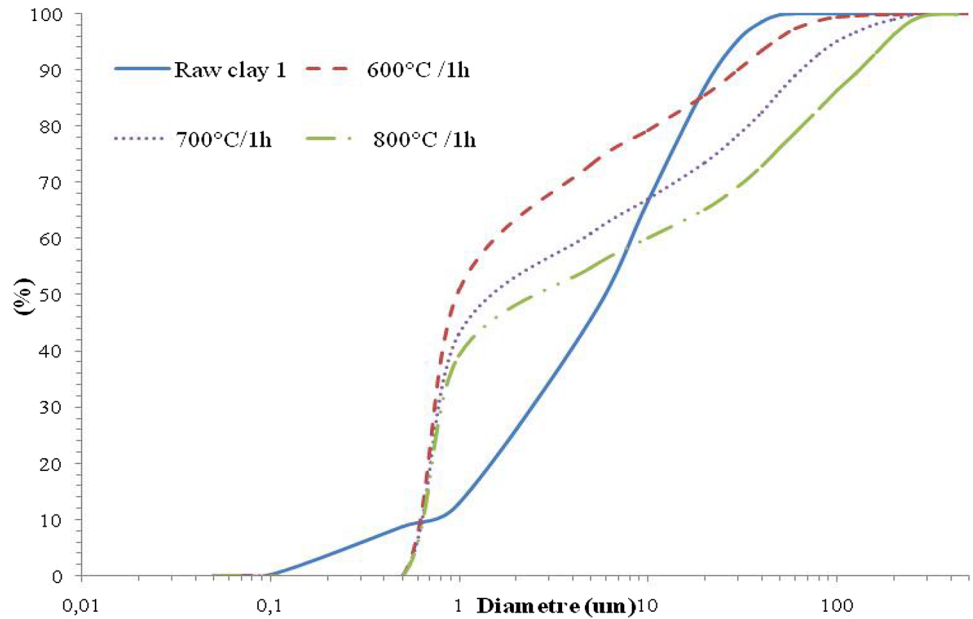


Fig. 8 Effect of calcination temperature on the granulometry of clay 2

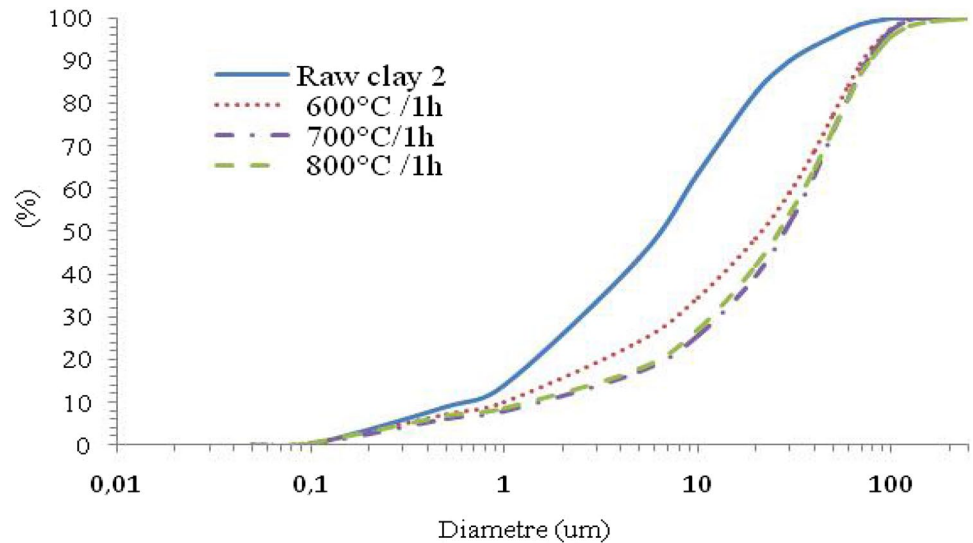


Table 4 Temperature effect on average particle diameter (D)

D (µm)	Raw	600 °C	700 °C	800 °C
Clay 1	5.79	0.96	1.82	2.95
Clay 2	6.29	22.69	22.51	25.15

400 and 600 °C. The fact that clay 1 has a de-hydroxylation peak in this temperature range means that it contains kaolinite which is very reactive after calcination [24].

Table 5 Chemical composition of calcined clays (clay 1)

% by mass	Clay 1	600 °C/1 h	700 °C/1 h	800 °C/1 h
SiO ₂	50.44	45.54	46.57	49.55
Al ₂ O ₃	20.25	16.71	17.39	19.66
Fe ₂ O ₃	14.4	11.11	11.15	12.74
Σ (SiO ₂ + Al ₂ O ₃ + Fe ₂ O ₃)	85.09	73.26	75.11	81.95
CaO	3.39	8.96	8.77	6.01
Glass content	47.05	36.58	37.8	43.54
MgO	2.5	1.81	1.87	1.9
SO ₃	0.39	1.84	1.8	1.22
K ₂ O	1.06	1.05	1.07	1.17
Na ₂ O	1.48	1.24	1.3	1.53
TiO ₂	1.64	0.03	0.03	0.03
Mn ₂ O ₃	0.06	–	–	–
CaCO ₃	–	13.7	13.4	9.2
LOT	3.39	13.8	10.25	5.63

Table 6 Chemical composition of calcined clays (Clay 2)

% By mass	Arg 2	600 °C/1 h	700 °C/1 h	800 °C/1 h
SiO ₂	45.02	46.9	48.49	49.24
Al ₂ O ₃	13.35	13.87	14.16	14.33
Fe ₂ O ₃	7.1	7.15	7.16	7.26
Σ (SiO ₂ + Al ₂ O ₃ + Fe ₂ O ₃)	65.52	67.92	69.81	70.83
CaO	11.36	11.3	11.37	11.36
Glass content	33.66	35.6	37.12	37.88
MgO	3.46	3.54	3.59	3.63
SO ₃	0.82	1.11	1.11	0.83
K ₂ O	1.49	1.51	1.53	1.56
Na ₂ O	0.45	0.47	0.47	0.49
TiO ₂	0.89	0.89	0.89	0.89
Mn ₂ O ₃	0.09	0.1	0.10	0.09
CaCO ₃	25.9	25.6	25.7	26
LOT	10.3	9.9	9.7	9.5

3 Methods and tests

3.1 Choice of calcination temperature

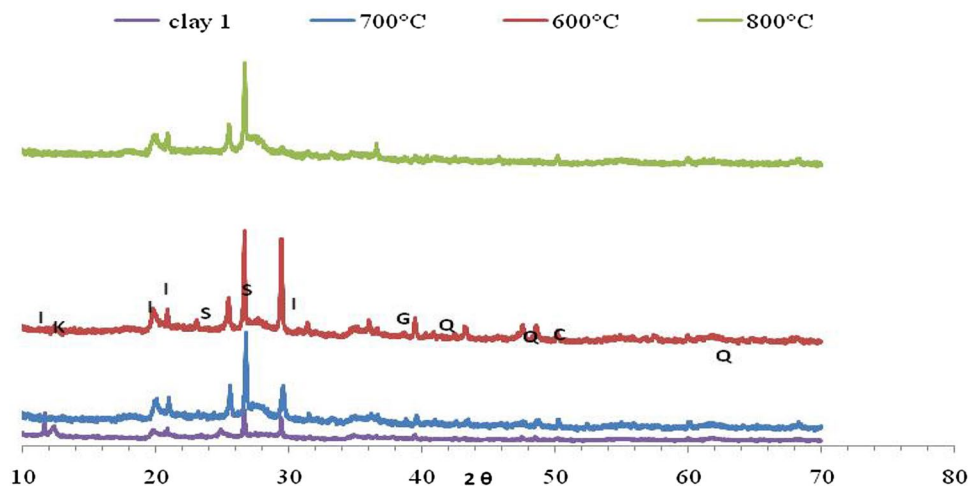
The sampled clays (1 and 2) were identified following an adequate experimental protocol. The calcination temperature was determined from the DTA / TGA curve (Figs. 5, 6). The range of the calcination temperature, which is located above the completion of the dehydroxylation peak and below the beginning of the recrystallization peak, can be predicted.

This temperature, which produces the activation of the clays, depends on the clay minerals. The properties of calcined clays depend on the nature and abundance of clay minerals in their raw material and the calcination conditions. Each raw clay has its calcination temperature.

Some authors have proved the existence of an activation temperature for each type of clay [5]. For example, this temperature is around 700 °C for kaolinite, 750 °C for palygorskite, 800 °C for montmorillonite and 850 °C for illite. kaolinite has the highest potential for activation and is therefore the most reactive. This is believed to be due to its high content of hydroxyl groups and their location in the crystal structure of the clay which promotes disorder and exposure of alumina groups during the dehydroxylation process. However, illite and montmorillonite seem to maintain the order of their structural layers even after complete dehydroxylation. In addition, the Alumina groups are trapped between the tetrahedral Silicate which hinders their reaction when hydrating the cement [11].

However, in order to examine the pozzolanic effect of a calcined clay and to study the effect of the variation of the calcination temperature, three temperatures were considered, namely 600, 700 and 800 °C for one hour

Fig. 9 Mineralogical transformation under the effect of temperature (clay 1) (I: illite, K: kaolinite, C: calcite, Q: quartz)



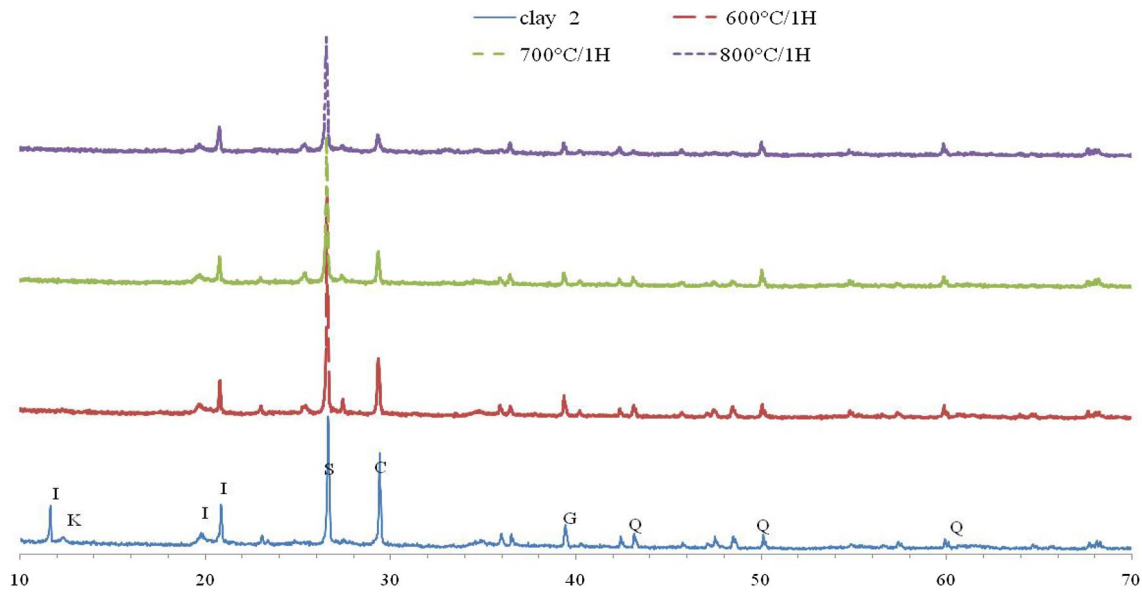


Fig. 10 Mineralogical transformation under the effect of temperature (clay 2) (I: illite, K: kaolinite, C: calcite, Q: quartz)

Table 7 The mortar compositions to prepare three prismatic specimen (4 * 4 * 16)

Material	Mass (g)
Sand	1350
Cement	450
Water	225
Calcined clay	% (5 and 20)

of calcinations in a static oven in the laboratory. As a result, the fraction less than 100 µm obtained by sieving of the crude clays was calcined.

3.2 Heat treatment effect

To control changes due to the heat treatment of calcined clays, physical properties, such as surface area, grain size curve, average particle diameter, Blaine surface area and pycnometer density were measured. The mechanical and the microstructure of mortars were studied.

4 Results and discussions

4.1 Physical properties

The results of the identification tests on clays sieved through 100 µm sieve and fired at 600, 700 and 800 °C., respectively, for one hour of calcination are summarized in Table 3. Laser particle size curves for different

temperatures are shown in Figs. 7 and 8. The average particle diameter increased with temperature increase (Table 4), confirming that heat treatment tends to agglomerate the particles together. Compared with the specific surface area of the cement (301.2 m²/kg), the calcined clays at the three calcination temperatures have a higher Blaine surface area.

4.2 Chemical and mineralogical properties

For a good pozzolanic addition, the ASTM C 618-98 requires that the total percentages of SiO₂, Al₂O₃ and Fe₂O₃ be greater than 70%. Thus, their quality is related to its glass content, which is the difference between the raw chemical content of silica and lime. This difference must be greater than a threshold value equal to 34%.

The chemical compositions of calcined clays at different temperatures are presented in Tables 5 and 6. As can be seen from the table, the percentages of SiO₂, Al₂O₃ and Fe₂O₃ of clay 2 raw and calcined at 600, 700 and 800 °C are 65.52%, 67.92%, 69.81% and 70.83%, respectively. These percentages are less than 70% for clay 2 calcined at 600 and 700 °C and are slightly higher than this percentage for that calcined at 800 °C. However, concerning clay 1, the total percentages of SiO₂, Al₂O₃ and Fe₂O₃ are equal to 85.09%, 73.26%, 75.11% and 81.95% for respectively the crude and clays calcined at 600, 700 and 800 °C.

According to their chemical compositions, the glass content for calcined clay 1 is greater than 34% and is slightly higher for clay 2. This means that clay 1 is more acidic and contains a vitreous phase. This means a better

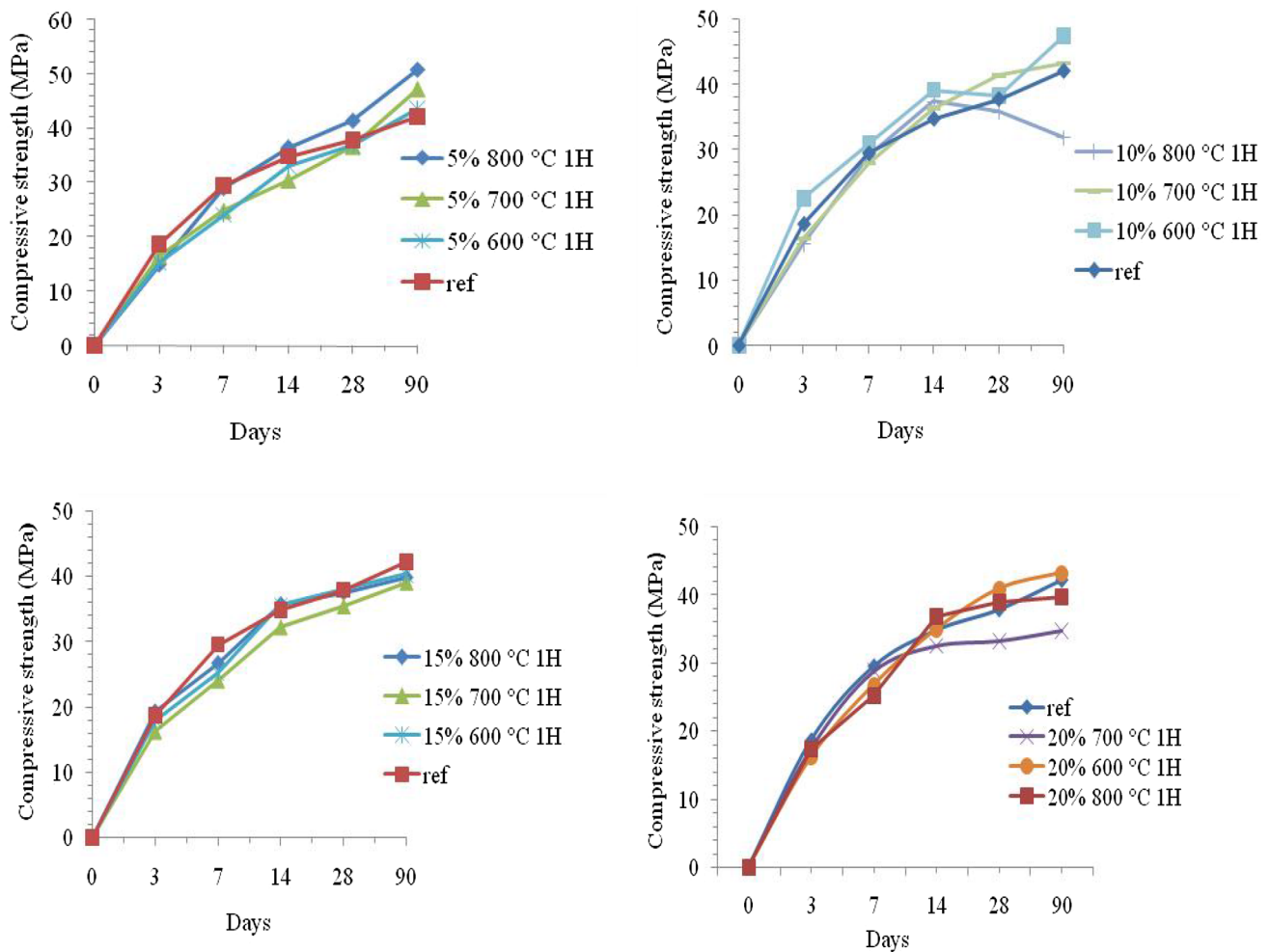


Fig. 11 Effect of calcination temperature on the mechanical strength of mortars with clay 1

possibility to fix the lime released by the cement. According to ASTM C 618-98, clay 2 does not satisfy the criterion of being a pozzolanic addition except for a calcination temperature equal to 800 °C.

In order to show the effectiveness of heat treatment on the calcined clays, the X-ray diffraction (XRD) curves were determined. The XRD patterns for crude clays (1 and 2) and those calcined at 600, 700 and 800 °C are displayed in Figs. 9 and 10. The presence of kaolinite in the raw clay indicates the possibility of having a good pozzolan [10].

Indeed, the heat treatment destroyed the crystalline structure of the starting clay minerals. De-hydroxylation of kaolinite can be considered complete at 600 °C. At this temperature, almost all the peaks corresponding to Kaolinite have disappeared and become Metakaolin in the amorphous state indicating a very significant loss of crystallinity. However, Illite and Smectite were not completely decomposed at 600 °C and remained intact. The calcination of clay 1 and 2 at 800 °C does not produce

much modification of the decomposed structure. Traces of quartz, whose structures have not been altered by temperature, can be identified.

4.3 Mechanical properties and pozzolanic activity

To evaluate the pozzolanicity of calcined clay 1 at different calcination temperatures, it is more relevant to compare their pozzolanic activity indices. Indeed, this index is defined as the ratio of the compressive strength of the mortar containing a percentage of calcined clay and that of the reference mortar (without addition). For this reason, the compressive strength of the mortar was measured on prismatic specimens (4 * 4 * 16) made in accordance with EN 196-1 (Table 7).

Figure 11 shows the effect of the calcination temperature on the mechanical strength measured on mortar with calcined clay 1. As can be seen from the figure, the mechanical strength varies slightly with the calcination

Table 8 Determination of pozzolanic activity index (I) of clay 1 and clay 2 calcined at 600, 700 °C and 800 °C

	I _{Clay 1} (600 °C)	I _{Clay 1} (700 °C)	I _{Clay 1} (800 °C)	I _{Clay 2} (800 °C)
5%				
3 days	0.79	0.92	0.76	0.80
7 days	0.82	0.94	0.98	0.98
28 days	0.98	0.94	1.09	1.09
90 days	1.04	0.98	1.17	1.20
10%				
3 days	1.15	0.92	0.96	0.83
7 days	1.04	1.00	0.99	0.99
28 days	1.19	1.01	1.12	0.95
90 days	1.13	1.00	1.13	0.76
15%				
3 days	0.91	0.96	0.98	1.03
7 days	0.86	0.83	0.9	0.90
28 days	1.01	0.96	0.99	0.99
90 days	0.96	0.95	0.94	0.94
20%				
3 days	0.82	0.75	0.88	0.93
7 days	0.91	0.78	0.85	0.85
28 days	1.08	1.00	1.02	1.02
90 days	1.02	0.90	0.94	0.94

temperature for different percentages of additions (5%, 10%, 15% and 20%). All samples showed the development of strength from 28 to 90 days. It increased by 18%, 29% and 19% for M(600 °C/5%), M(700 °C/5%) and M(800 °C/5%) respectively. For M(600 °C/10%), M(700 °C/10%) and M(800 °C/10%) strength increased by 6%, 5% and 12% respectively and by 6%, 10% and 6% for M(600 °C/15%), M(700 °C/15%) and M(800 °C/15%) respectively. An increase of 6%, 3% and 2% was obtained

for M(600 °C/20%), M(700 °C/20%) and M(800 °C/20%) respectively.

Therefore, clay minerals can be good pozzolanic materials when they are thermally activated.

The compressive strength of clay 1 seems to be little influenced by the variation of the temperature between 600 and 800 °C; however, it reaches its maximum for the case of 600 °C at 90 days. It varies in the same time zone with the reference mortar. Thus, substitution of cement with calcined clay has led to a considerable increase in strength. This increase is explained by the characteristic of pozzolan that combines with calcium hydroxide (CH) to form an additional calcium silicate hydrate (C-S-H) that fills the pores and thus increases the mechanical properties.

To compare the pozzolanicity of clay 1 calcined at 600, 700 and 800 °C and clay 2 calcined at 800 °C, their pozzolanic reactivity was studied by calculating the index of the pozzolanic activity on prismatic specimens of mortars, which is the ratio of compressive strength of mortars with pozzolanic addition to that without addition (ASTM C618). Table 8 presents the index of the pozzolanic activity of calcined clays. Accordingly, the pozzolanicities of the two clays are slightly different. To have a good pozzolanic addition, the pozzolanic activity index at 28 days should be higher than 75% [17]. This is verified with all percentage of addition. The pozzolanic reactivity index of calcined clay 1 was higher at 600 °C for 10, 15 and 20% addition. But it was higher at 800 °C for 5% addition. The pozzolanic reactivity index of clay 2 calcined at 800 °C was higher for 5% addition.

4.4 Electrical conductivity

The electrical conductivity of a solution makes it possible to estimate its charge in ions. A conductivity meter (Tetra-Cond Cell) is usually used to measure its value (Fig. 12). It is expressed in mSiemens/cm. The electrical conductivity



Fig. 12 Measurement of the electrical conductivity of cement solution with addition

Table 9 Measurement of electrical conductivity for different percentage (cement/calced clay) at different temperatures

T	%	σ (mS/cm) (clay 1)	σ (mS/cm) (clay 2)
600	5	9.91	9.58
	10	9.52	9.17
	15	9.27	9.27
	20	8.78	8.16
	100	5.02	2.23
700	5	10.14	10.06
	10	9.99	9.48
	15	9.52	8.7
	20	9.23	8.4
	100	3.89	1.64
800	5	9.98	9.52
	10	9.83	8.97
	15	9.62	8.47
	20	8.97	8.12
	100	1.84	1.27
Cement	0	10.84	10.2

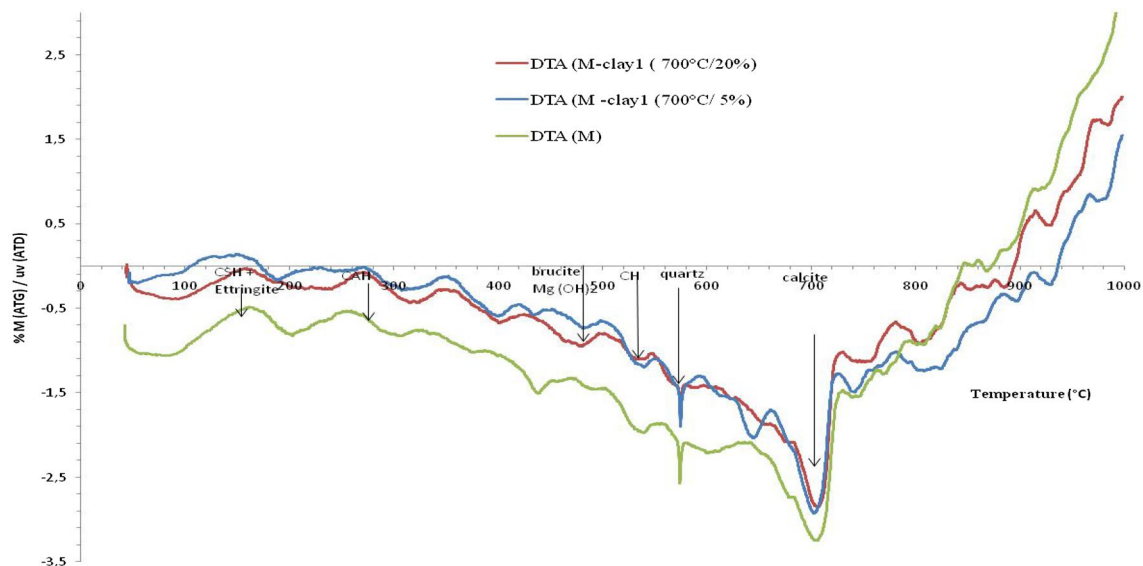
of the pure cement solution (Table 9) is slightly higher than that of the mixture with calcined clay 1 and 2 for 5% and 20% substitutions. This phenomenon seems logical because there is more cement which, by hydration, provides more conductive ions than the pozzolanic addition.

4.5 Microstructure of mortars with additions

The amount of CH decreased with the addition of calcined clays (1) and (2) for mortars (Figs. 13, 14). Although DTA shows that CH is still present at an age greater than 90 days, it is more finely divided and reacts with pozzolan to form C-S-H [11].

It is noted that the intensity of the CH peaks of mortars with 5% of calcined clay 1 at 700 °C is lower than that of mortar with 20% substitution (Fig. 13). Hence, clay 1 calcined at 700 °C is more reactive for 5% addition and this is confirmed by the compressive strength at 90 days (Fig. 15). Furthermore, it is noted that the intensity of the CH peaks of mortars with 20% of clay 1 calcined at 600 °C and at an age greater than 90 days is lower than that of mortars with clay 1 calcined at 700 °C and 800 °C (Fig. 14). Thus, clay 1 is more reactive at 600 °C and this is confirmed by the compressive strength at 90 days (Fig. 16).

The property of rapid consumption of CH may also be due to the appearance of surface defects of the calcined clay during calcination. If the hydroxide content remains high, only cement reacts with water and thus the calcined clay is not reactive. If, on the contrary, the amount of CH decreases, it means that the calcined clay reacts by consuming CH. Clay 1 has a significant pozzolanic reactivity since the amount of CH in concretes decreases systematically more than in the reference sample (100% cement) [11, 24].

**Fig. 13** DTA of mortars with clay 1 calcined at 700 °C (5% and 20%)

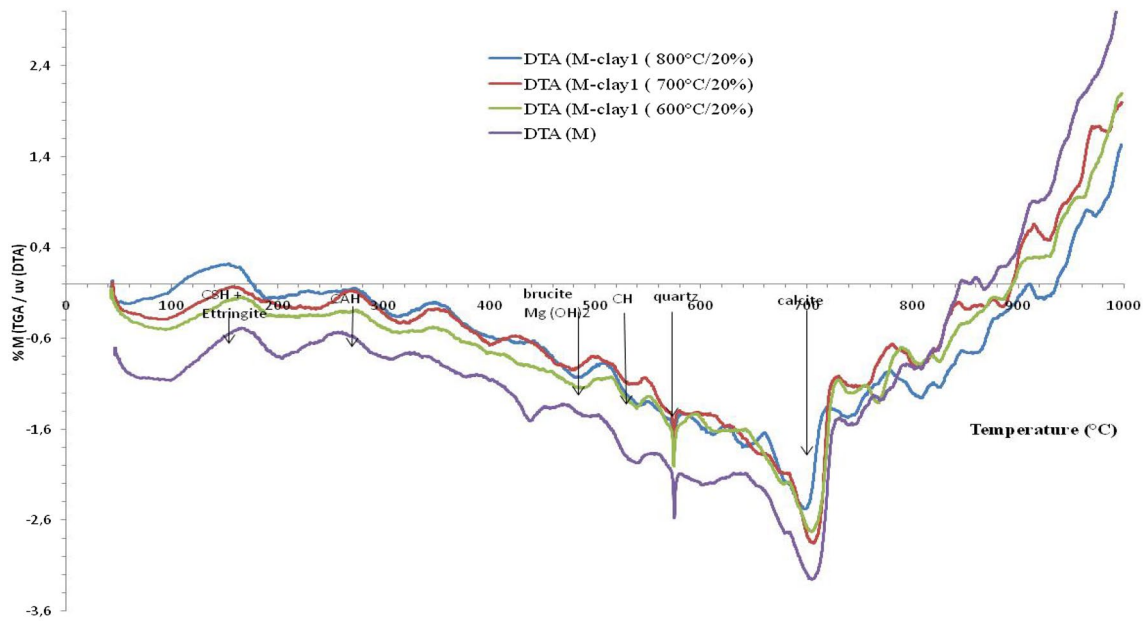


Fig. 14 DTA of mortars with clay 1 calcined at 600 °C, 700 °C and 800 °C (20%)

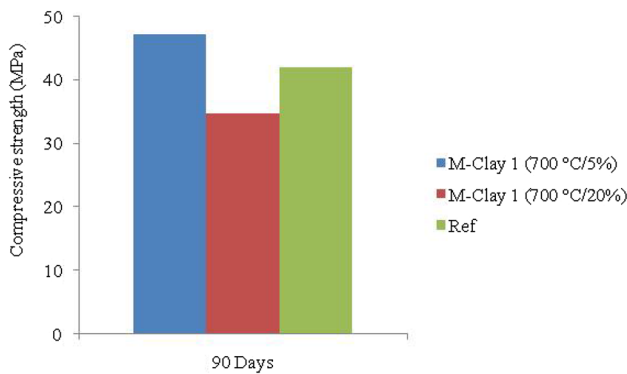
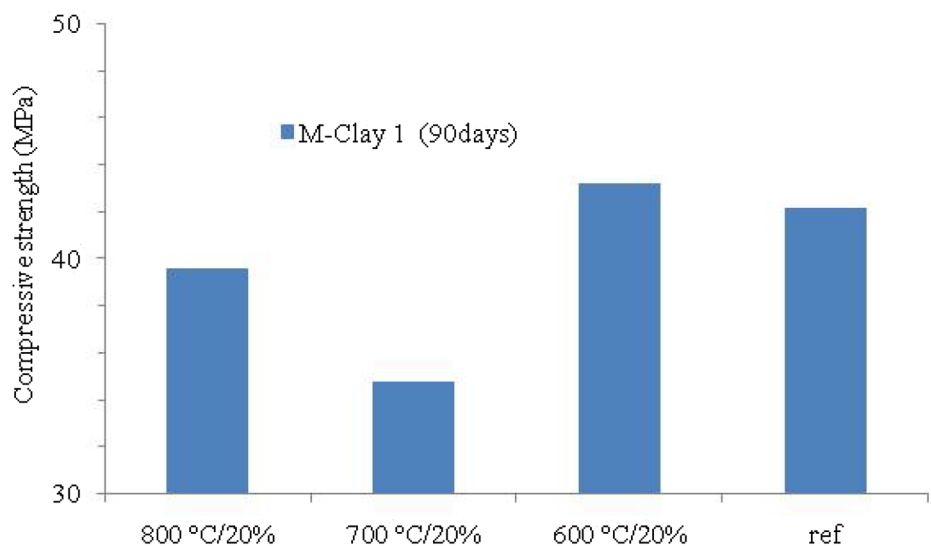


Fig. 15 Compressive strength of mortars with clay 1 calcined at 700 °C (5% and 20%)

Fig. 16 Compressive strength of mortars with clay 1 calcined at 600 °C, 700 °C and 800 °C (20%)



However, during the hydration period, the CH was rapidly consumed and the microstructure was rich in CSH and Ettringite which increase with the addition and which are responsible for the increase in strength.

In fact, the decrease in compressive strength compared to mortars without addition is caused by the reduction in the amount of cement and the slow rate of dissolution of silica. As the silica increases in the solution, CSH is formed and the compressive strength increases as well [12]. The improvement in strength over time is due to the formation of new CSH and CAH which have binding properties similar to those formed from cement [25]. Any substitution of material, regardless of its pozzolanic properties, induces a filling effect in

mortars [11]. The highest rate of pozzolanic reaction in mortars with a lower level of replacement can be attributed to its speed in the matrix with a lower percentage of substitution [25].

5 Conclusion

Based on the analysis of the physical, mechanical properties and microstructure of mortars with two calcined Tunisian clays, the following conclusions can be drawn:

- The average particle diameter increased with temperature increase confirming that heat treatment tends to agglomerate the particles together.
- Substitution of cement with calcined clay has led to a considerable increase in strength. This increase is explained by the characteristic of pozzolan that combines with calcium hydroxide (CH) to form an additional calcium silicate hydrate (C–S–H), which fills the pores and thus increases the mechanical properties.
- All samples showed the development of strength from 28 to 90 days.
- The pozzolanic reactivity index of calcined clay 1 was higher at 600 °C for 10, 15 and 20% addition. But it was higher at 800 °C for 5% addition. The pozzolanic reactivity index of clay 2 calcined at 800 °C was higher for 5% addition.
- It is noted that at 90 days the intensity of the CH peaks of mortars with 5% of calcined clay 1 at 700 °C is lower than that of mortar with 20% substitution. Clay 1 calcined at 700 °C is thus more effective with 5% addition.
- It is noted that at 90 days and with 20% of addition, the intensity of the CH peaks of mortars with clay 1 calcined at 600 °C is lower than mortars with clay 1 calcined at 700 and 800 °C. Clay 1 is therefore more reactive at 600 °C.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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