Shrinkage and mechanical performance of geopolymeric mortars based on calcined Tunisian clay

W. Tahri[1], B. Samet[1], F.Pacheco-Torgal[2], J.L. Barroso de Aguiar[2], C. Jesus[2] , S. Baklouti[1]

[1]University of Sfax, Laboratorial of Industrial Chemestry, Sfax, Tunisia
[2]University of Minho, C-TAC Research Centre, Guimarães, Portugal

Abstract. Infrastructure rehabilitation represents a multitrillion dollar opportunity for the construction industry. Since the majority of the existent infrastructures are Portland cement concrete based this means that concrete infrastructure rehabilitation is a hot issue to be dealt with. Geopolymers are novel inorganic binders with high potential to replace Portland cement based ones. Geopolymerization is a complex chemical process evolving various aluminosilicate oxides with silicates under highly alkaline conditions, yielding polymeric units, similar to those of an aluminosilicate glass. So far very few studies in the geopolymer field have addressed the rehabilitation of deteriorated concrete structures. This paper discloses some results of an investigation concerning the development geopolymeric repair mortars based on a calcined Tunisian clay. The results show that Tunisian calcined clay based mortars have hydration products with typical geopolymeric phases. Results also show that the geopolymeric mortar shows a high unrestrained shrinkage behavior and that its modulus of elasticity is below the threshold required for this repair mortars.

1 Introduction

Worldwide infrastructure rehabilitation costs are staggering. For example in the USA the needs are estimated to be over 1.6 trillion dollars over the next five years [1].

Many of the degraded concrete structures were built decades ago when little attention was given to durability issues [2].

Materials with low durability require frequent maintenance and conservation operations or even its integral replacement, being associated with the consumption of raw materials and energy. The patch repair method is widely used to restore the original conditions of the concrete structures [3, 4].

Most patch repair mortars fall into two categories, the mortars based on organic binders (epoxy resin or polyester) or those based on inorganic binders like Portland cement. The former are associated with toxic side effects [5] as to later is know for its high carbon footprint [6].

Geopolymers are novel inorganic binders with high potential to replace Portland cement based ones [7].

The geopolymerization of alumino-silicate materials is a complex chemical process evolving dissolution of raw materials, transportation or orientation and polycondensation of the reaction products [8-10].

Investigations in the field of geopolymers reveal a third category of mortars with potential to be used in the field of concrete patch repair [11].

Some authors [12] have shown that concrete specimens repaired with geopolymeric mortar with 1 day curing have higher bond strength than specimens repaired with current commercial repair products after 28 days curing. This is a promising performance because adhesion to the concrete substrate is a crucial property of the repair mortars [13].

This paper presents experimental some results of an investigation concerning the development geopolymeric repair mortars based on a calcined Tunisian clay.

2 Experimental work

2.1 Materials

The clay materials used originate from Medenine Region of Tunisia. Previous studies done on many clay materials showed that kaolinite is the major mineral and quartz the major impurity.

The dried clay fractions were crushed in a mortar and then sieved to 100 μm. The clay fractions were calcined in a programmable electric furnace (Nabertherm, Mod.LH 60/14) for 6 h at a heating rate of 11.33 C/min at the following temperature 700 °C.

Results of chemical composition of the clay fractions are given in Table 1. Figure. 1 presents the X-ray diffractograms of the natural clay (NC).

Table 1. Chemical composition of the natural clay (NC)

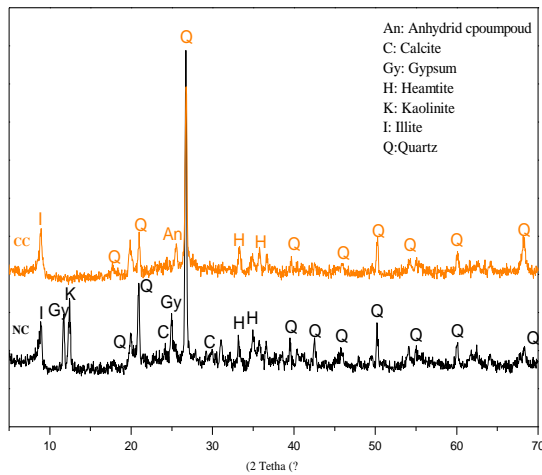| Oxides	%
SiO_2	60.8
Al_2O_3	16.2
CaO	2.15
F_2O_3	5.87
SO_3	0.08
K_2O_3	2.71
MgO	2.38
Na_2O_3	0.003
PF	9.16

Fig.1. X-rays diffractograms of the raw material NC and calcined at 700°C (CC)

It is shown in figure. 1 that the basic clay mineral in the clay fractions is kaolinite associated to quartz, illite, gypsum and hematite as impurities. Quantitatively, the diffractogram confirms that clay have a lower kaolinite content. The diffractogram exhibit the characteristic peaks of illite (8,8°).

The overall result shows that the thermal treatment of the clay fractions at 700°C is enough to transform kaolinite into metakaolinite which is in agreement with the thermal analyses (DSC and TG) results which show that the dehydroxylation of kaolinite starts from around 480°C. The difference between natural clay and calcined clay seems to be connected with the presence of a clay mineral like kaolinite which transforms into metakaolinite after calcination.

In the X-ray diffraction patterns of the calcined clay, we have noticed the disappearance of the kaolin peaks and their change to metakaolinite. There is a general broadening of the kaolinite peaks which indicates that some claylike disordered phases form, but they lack the crystallinity of kaolinite.

After, calcination the kaolinite disappeared but illite almost remains intact and appeared with some traces. It means that the calcination is not completed.

On the other hand, after calcination of gibbsite; it was transformed into an anhydrous compound ($CaSO_4$). Figure 2, presents DSC and TG curves of the clay fractions of NC.
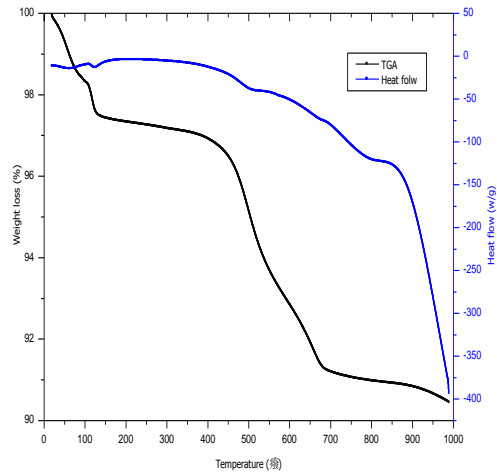

Fig. 2. TGA/ DSC of natural clay NC

They show the thermal behaviour typical of kaolinite clays [14,15]. The interval [0°C to 120°C] showed the period of drying of the raw material which consisted to the disappearance of the water molecules. From [400°C to 500°C], the kaolinite changed into giving the new metakaolinite phase. Also from 600°C to 800°C, the raw material undergoes a reaction of carbonation with the atmospheric CO_2 gas.

The SEM analysis (Fig 3) shows the morphology of the raw material, which consisted of major mineral clay kaolinite layers.
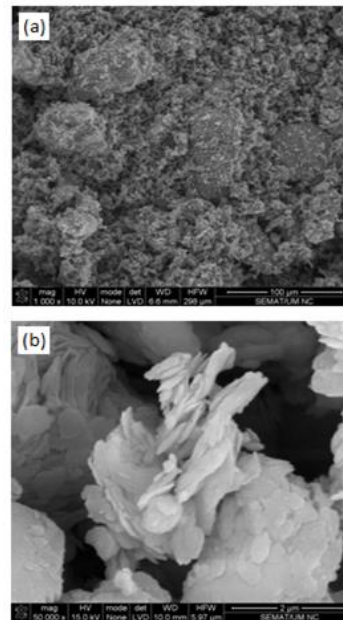

Fig. 3. Morphology of the natural clay NC (a) and (b)

This transformation of kaolinite into metakaolinite produces a more reactive material. This result was confirmed by the infrared spectra of raw material NC after and before calcination (Figure 4)
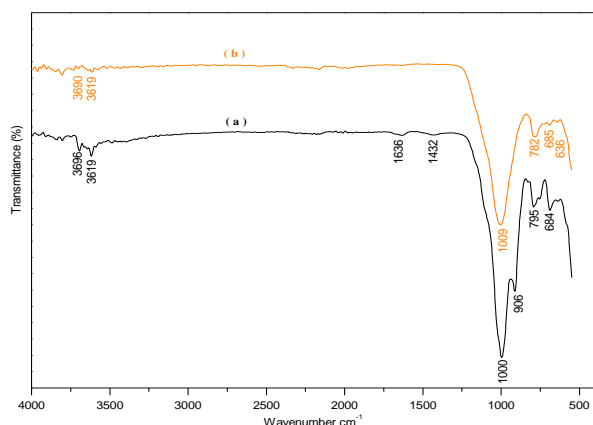
Fig. 4. FTIR spectra of raw material:
(a) to natural clay NC, (b) calcined clay CC

FTIR spectra of the calcined clay fractions, it is clearly established that this temperature is not sufficient to break the crystalline structure of kaolinite into metakaolinite. In fact, the characteristic absorption bands of kaolinite are present (3693–3619 cm^{-1}) [16].

In addition, these bands disappeared after thermal treatments which were confirmed by XRD of clay. This shows that the later step was the destruction of the structure eventually leading to formation of an amorphous phase called metakaolinite.

2.2 Mix proportioning and synthesis

The alkaline solution used was a mixture of aqueous solution of sodium hydroxide 12 M and sodium silicate with bulk density of 1350 kg/m^3 with ratio: Na_2SiO_3 / NaOH = 2.5. The sodium hydroxide solution was obtained by dissolving dried pellets of 99% purity in distilled water. The sodium silicate solution had a composition by weight $Na_2 (SiO_2)_x . y (H_2O)$. With $3.19 \leq x \leq 3.53$ and 50 % $\leq y \leq 60$ %. The geopolymer mortar consisted of a mixture of alkaline solution with powdered calcined clay fractions. The assembly was mixed in a Hobart mixer for 3 min. The sample of geopolymer mortar was vibrated vibrating table to remove entrapped air bubbles. During the hardening of the geopolymer samples, the molds were covered with a thin plastic film to avoid water evaporation and then kept for 24 h at the ambient atmosphere of the laboratory (24 °C to 26 °C). After measurement of the compressive strength, certain fragments of geopolymer paste samples were kept for XRD, FTIR, ATG, DSC and SEM analyses. Table 2 shows the composition of the geopolymeric mortars.

Table 2. Mixture quantities

Mix.	Calcined Clay (g)	Lime (g)	Sand (g)	Activator (g)		(Lime+ Calcined clay)/sand
				Na₂SiO₃	NaOH	
G1R2	674	74,8	1496	535	213	1:2
G1R3	674	74,8	2250	535	213	1:3
G1R4	674	74,8	2992	535	213	1:4

2.3 Workability

The workability assessment has been conducted with a truncated conical mould and a jolting table according to the EN 1015-3.

2.4 Unrestrained shrinkage

Unrestrained shrinkage used prismatic specimens measuring 250 * 25 * 25 mm^3 and was determined according to LNEC E398-1993. The specimens are removed from molds 24 h after being mixed and placed, then they are wrapped with Perspex paper. Other authors used aluminum paper, having reported the formation of hydrogen gas bubbles due to a reaction between the aluminum and the alkalis from the mortar [17]. The measurement of shrinkage was carried out on hardened geopolymer cylinder paste samples aged of 1, 7, 14, 21 and 28 days respectively.

2.5 Compressive strength

Compressive data was obtained using 160×40×40 mm^3 cubic specimens according to EN 1015-11. The fresh mortar were cast and allowed to set at room temperature for 24h before being removed from the moulds and kept at room temperature (20 °C) until tested in compression. Compressive strength for each mortar mixture was obtained from an average of 3 specimens from those broken in flexure. The compressive strength was determined on the hardened geopolymer paste samples aged of 28 days using an electrohydraulic press (M & O, type 11.50, N °21) at an average rate of 3 mm/min.

2.5 Modulus of elasticity

The modulus of elasticity was determinate using cylindrical moulds for the geopolymeric sample with (Diameter: 5 cm; Length: 10cm). These specimens were tested after curing time (28 days). The values of modulus of elasticity were determinate from the overage of three specimens.

3 Figures and tables

3.1. Workability

Figure 4 shows that the flow diameter for the three mixtures decreases with the sand mass.
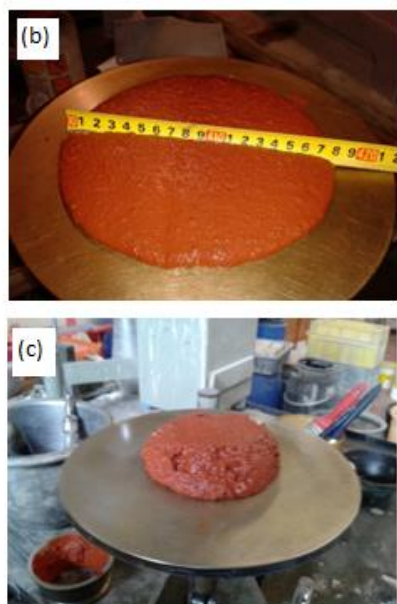
Fig. 4. Flow of three types geopolymeric mortars:
(a) G1R1, (b) G1R3, (c) G1R4

The mixture with a binder/sand ratio of 1:2 has an excessive flow (23cm) while the mixture with a binder/sand ratio of 1:3 has a flow (18 cm) more currently found in most mortars. The mixture with a binder/sand ratio of 1:4 seems to have a low flow diameter. However, it is acceptable when using the hand placement technique in which higher flows are not desirable to avoid detachment risks.

3.2. Unrestrained shrinkage
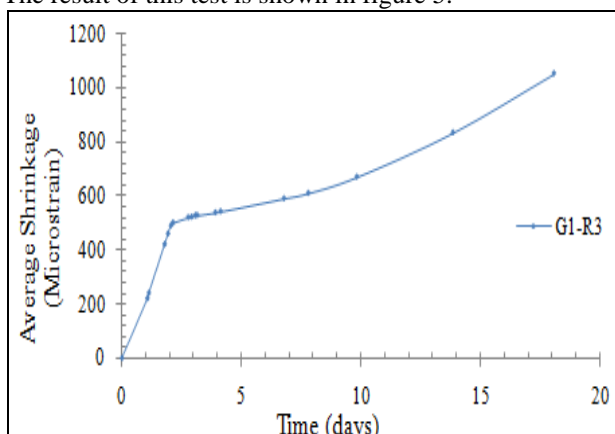
The result of this test is shown in figure 5.

Fig. 5. Shrinkage of the mixture with a binder/sand ratio of 1:3 as function of curing time (days)

In the first two days the shrinkage increases very rapidly. Since the test has been carried with the isolation of specimens with a perspex film to avoid the evaporation of water, the measured shrinkage is the due to hydration reaction (autogenous shrinkage). Thus the rapid increase in the first two days has to do with the capillary tensions within the gel framework during geopolymerization [18]. Other authors [19] that used alkali activated metakaolin based binders in similar experimental conditions,

reported shrinkage results between 500 a 840 microstrain.

Since mortars required for OPC patch repair require very low shrinkage [20] this means that new geopolymeric mortar mixtures with lower activator/binder ratio.

3.3 Compressive strength

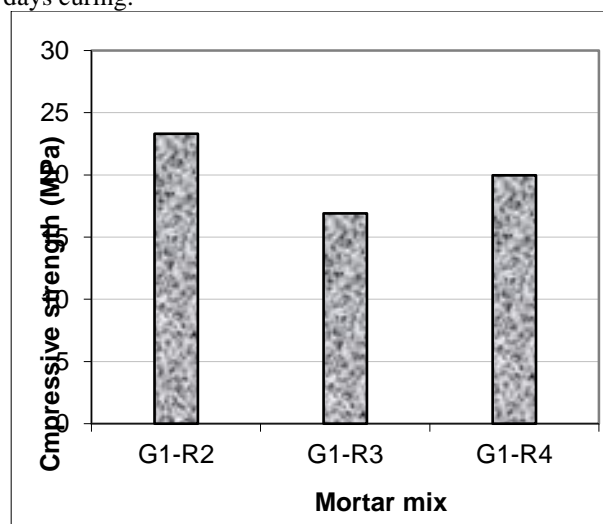Figure 6 shows the compressive strength results at 28 days curing.

Fig. 6. Compressive strength for geopolymeric mortar mixtures with sodium hydroxide concentrations (12 M) and sand/binder mass ratios (R=2; R=3,R=4).

Although it seems that the compressive strength is influenced by the sand/binder mass ratio the differences are very slight and fall in the standard deviation interval. The compressive strength at 28 days curing is below typical compressive strength of old OPC reinforced concrete structures in which 20-30 MPa could be expected. Thus meaning that repair mortars should have at least 30 MPa. New mixtures mixtures based on be evaluated having a lower activator/binder ratio. Other authors [21] analyzed mortars with the same activator/binder ratio and the same 12 M sodium hydroxide concentration obtaining a 40MPa compressive strength just after 7 days curing however they used metakaolin as binder which is much more reactive than the calcined Tunisian clay used in this investigation. Mixtures with a small replacement of calcined Tunisian clay by metakaolin should also be analyzed for compressive strength.

3.4 Modulus of elasticity

The modulus of elasticity of the mixtures with a binder/sand ratios of 1:3 and 1:4 are respectively 1GPa and 0.82 GPa. Although this values are very different from typical OPC based binders they bear some resemblance with the ones reported by other authors for the same compressive strength [22, 23].

The modulus of elasticity at 28 days curing is below typical modulus of elasticity of OPC reinforced concrete

structures. For a concrete substrate with a 25MPa compressive strength at 28 days and using the EN 1992-1-1 European code [24] expression :

$$E_{cm} = 22[(f_{cm})/10]^{0.3} \qquad (1)$$

to predict modulus elasticity one obtains a value of 29 GPa.

Therefore, in order to meet structural compatibility requirements new mixtures with a modulus of elasticity around 29 GP must be developed. It is expected that new higher compressive strength mixtures should have higher modulus of elasticity as much as of the OPC substrate.

4 Conclusions

Worldwide infrastructure rehabilitation costs are staggering. Since the majority of the existent infrastructures are concrete based this means that concrete infrastructure rehabilitation is a hot issue to be dealt with. This paper presents experimental some results of an investigation concerning the development geopolymeric repair mortars based on Tunisian clay. The following conclusions can made upon it:

- The mineralogical analysis shows that the Tunisian clay is composed of kaolinite associated to quartz, illite, gypsum and hematite as impurities.
- The use of a geopolymeric mortar with a binder/sand ratio of 1:4 meets minimum workability conditions for patch repair using the hand placement technique
- The geopolymeric mortar shows a high unrestrained shrinkage behavior.
- The compressive strength at 28 days curing is below typical compressive strength of reinforced concrete structures.
- The modulus of elasticity is below the threshold required for this repair mortars
- Higher mechanical strength and higher modulus of elasticity mixtures are needed
- New mixtures with lower activator/binder ratio must be studied

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