Full Length Research Paper

Study of calcined halloysite clay as pozzolanic material and its potential use in mortars

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In this research, we will try to understand the mechanisms involved in the introduction of calcined clays in substitution for a portion of cement in the manufacture of mortars. This experimental work focuses on the recovery of a clay type haloysite quality three, from eastern Algeria. This clay comes from a region called Djbel Debbagh hence its name (DD3). The main objective of this study is to see the influence of the activated clay by calcination with different percentages of 5, 10, 15 and 20% in substitution of cement, on the physical-mechanical properties and behaviour of mortars towards chemical attacks. The study of pozzolanic activity allows to optimize a calcinations temperature of about 750°C, the study of its mechanical performance has shown an improvement of strength. Finaly the results of the durability test showed a good performance in different environments.

Key words: Valorization, clay, mortar, temperature, pozzolanic activity, durability.

INTRODUCTION

Since the invention of cement material, research has continued in the field of construction to make structures more resistant, more durable and also more economic. Finding the material substitution most consistent has become the biggest challenge facing the blended cements based on industrial by-products/pozzolanic materials, fly ash, calcined clays, ground granulated blast-furnace slag, are known for their strength and long life term improvement (Pandey et al., 2003; Chakchouk et al., 2006; Samet and Chaabouni, 2004). Infact these materials are obviously pozzolanic in nature, also there are others that appear in this nature merely after adequate traatment, usually heat such as clays (Frachebourg, 1965; Mostafa et al., 2001; Rodrigo, 2009a; Mertens et al., 2009). Currently clay is used, either unprocessed or after undergoing treatment. The various treatments are between bypass and activation, and several researcher has undertaken researches on

this (Ahmed Tafraoui et al., 2009; Zhang and Malhotra, 1995). The compressive strength of mortars incorporating calcined clays containing kaolinite were similar or superior to that of Rodrigo (2009b). Curcio et al. (1998) have shown that mortars based around metakaolin were giving similar resistance after 90 days compared to those prepared with silica fume; the effect of metakaolin was evident especially long-term perspective of sustainability. The advantages of partial replacement of cement with pozzolanic materials are different; they are involved in strengthening the resistance to chemical attack, they reinforce the impermeability and durability of the mortar, and they reduce the alkali-aggregate reactions and removal of mortar drying (Bai et al., 2003). Rafat and Juvas (2009), conclude that partial replacement of cement with metakaolin reduces the water penetration into concrete by capillary action and helps in enhancing the early age mechanical properties as long-term strength properties of cement paste/mortar/concrete.

The material used in this work is clay DD3 which means clay extracted from a region named Djbel Debagh, this clay has excellent properties with its high

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Table 1. Chemical composition of cement and clay (DD3).

Element	SiO$_2$	Al$_2$O$_3$	MnO	SO$_3$	CaO	F$_2$O$_3$	Na$_2$O	K$_2$O	TiO$_2$	MgO	I.loss	Total
Clay (DD3)	43.60	46.87	1.34	0.45	0.20	0.12	0.12	0.11	0.02	0.07	7.43	100.33
CEMI	21.82	6.13	/	0.17	65.82	2.12	0.10	1.43	/	1.29	0.80	99.68

Table 2. Mineralogical composition of cement.

Mineral	C$_3$S	C$_2$S	C$_3$A	C$_4$AF
CEMI	21.82	6.13	/	0.17

Table 3. Physical properties of cement, clay (DD3) and sand.

Property	CEMI	Clay (DD3)	Sand
Specific surface Blaine SSB (cm^2/g)	4291	5600	/
Specific gravity, SG (g/cm^3)	3.1	2.48	2.56
Visual equivalent of sand, VES (%)	/	/	80
Finesse module, Fm	/	/	2.6
The normal consistency NC (%)	25.8	/	/
The start making SM (mn)	210	/	/
The final setting FS (mn)	337	/	/

content of alumina and silica, however, its use in high-quality ceramics is limited because it contains a high manganese percentage 1.34%, which gives it a grayish color and thus limits its use. Several researchers suggest its use for the manufacture of refractories. Koli et al. (2007) have evolved in refractory properties were conducting cylindrical samples by pressing, they were calcined at different temperatures, after a series of tests they could conclude that the use of refractory elaborated with DD3 clay should be limited at 900°C.

On the other side Benmakhlouf et al. (2008) have done work that is to measure the glass phase by adding alumina to increase the rate of mullite in the refractory made from DD3, through this work they confirm with 50% alumina was a total disappearance of the glassy phase to 1600°C.

The research suggested in this work is to see the influence of partial substitution of cement by synthesized pozzolane from clay type halloyisite quality three (DD3), on the physical-chemical and mechanical properties the durability in differents aggressive environments of mortar based on this calcined clay.

EXPERIMENTAL PROGRAM

Materials used

All samples were prepared with a composition comprising a cement CEM I, developed in laboratory, consisting of 95% clinker and 5%

gypsum, from Saida cementer, ground simultaneously. The sand used is from the carrier in the region of Tizi (Mascara). The addition used in our study for making pastes and mortars is clay DD3 debater from Guelma region.

Chemical compositions of cement, clay (DD3) and mineralogical composition of cement are listed in Tables 1 and 2.

The physical properties of different materials used in this work are listed in Table 3. The granulometric analysis of sand is represented in Figure 1.

Clay of Djbel Debegh DD3

The use of DD3 clay is halloysite, that is to say it is formed by alteration of kaolinite, the kaolin are primary clay formed by decomposition of feldspar in place where we found deposited in pockets, laminated, they are relatively free of mineral impurities such as iron, containing a low manganese gives them a grayish color. A detailed characterization of this clay is presented as follows: Chemical analysis of the sample of DD3 clay indicates a high content of alumina (46.87% Al$_2$O$_3$) and SiO$_2$ content exceeds 43% of 1.34% manganese (MnO).

Mineralogical composition

The diffractogram RX over the sample of DD3 clay indicates that halloysite and kaolinite are the dominant minerals (Figure 2), calcite was also identified. Quartz and illite are present with small amounts.

Analysis by electronics microscope

The SEM photo is shown in Figure 3, which shows that the clay used consists of a tubular structure, fibrous does not reflect a
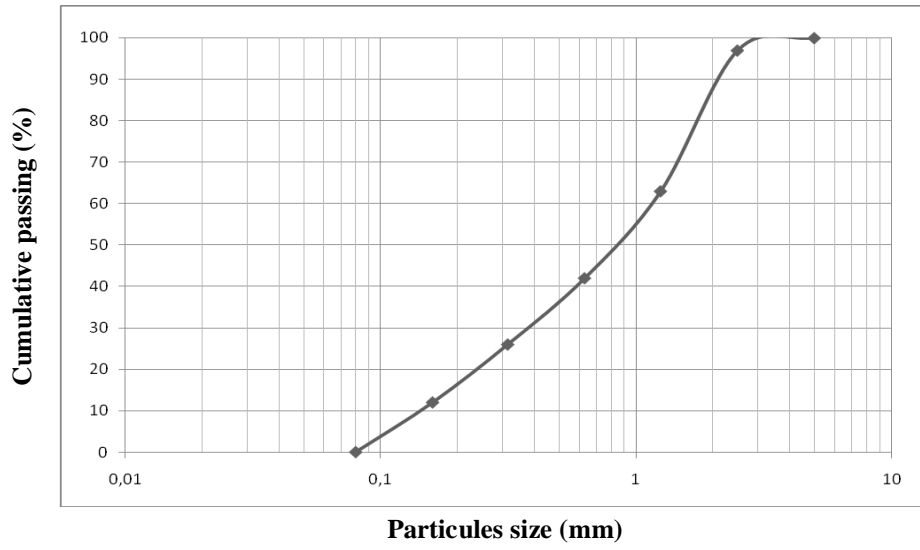
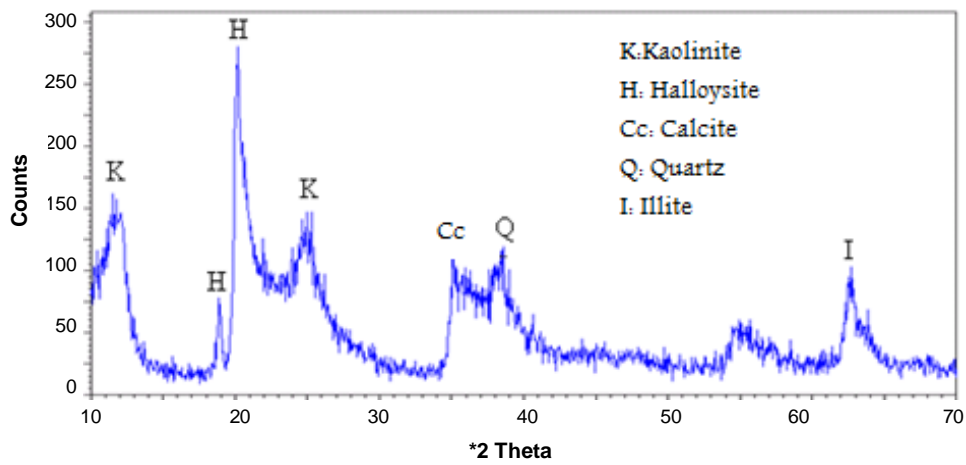**Figure 1.** Granulometric analysis of sand.
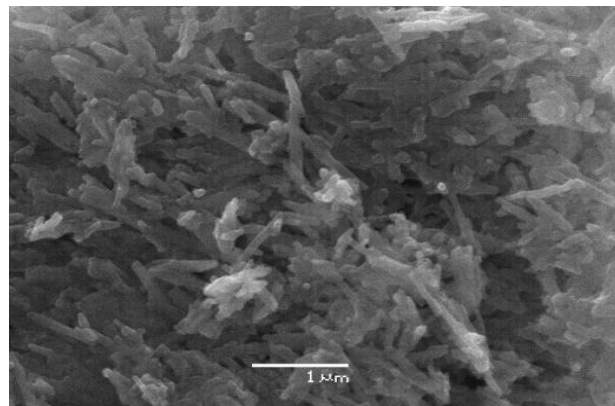

Figure 2. Mineralogical analysis by XRD of DD3.
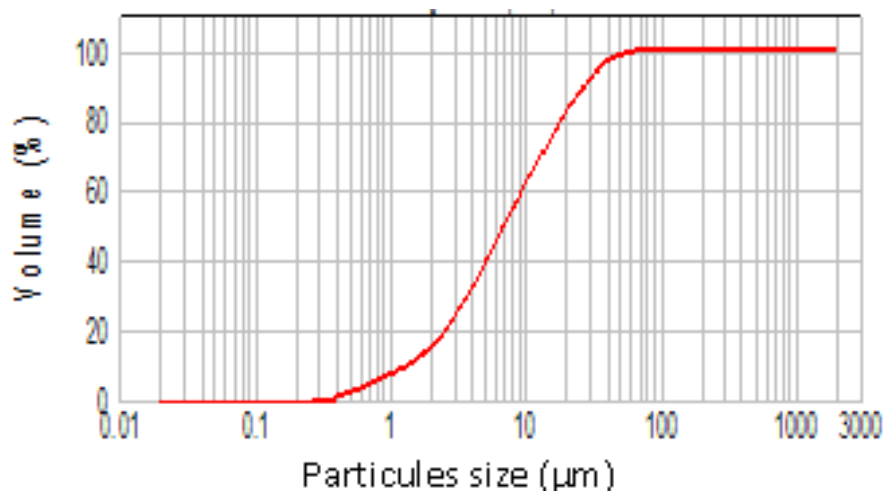

Figure 3. Microstructure of clay (DD3).

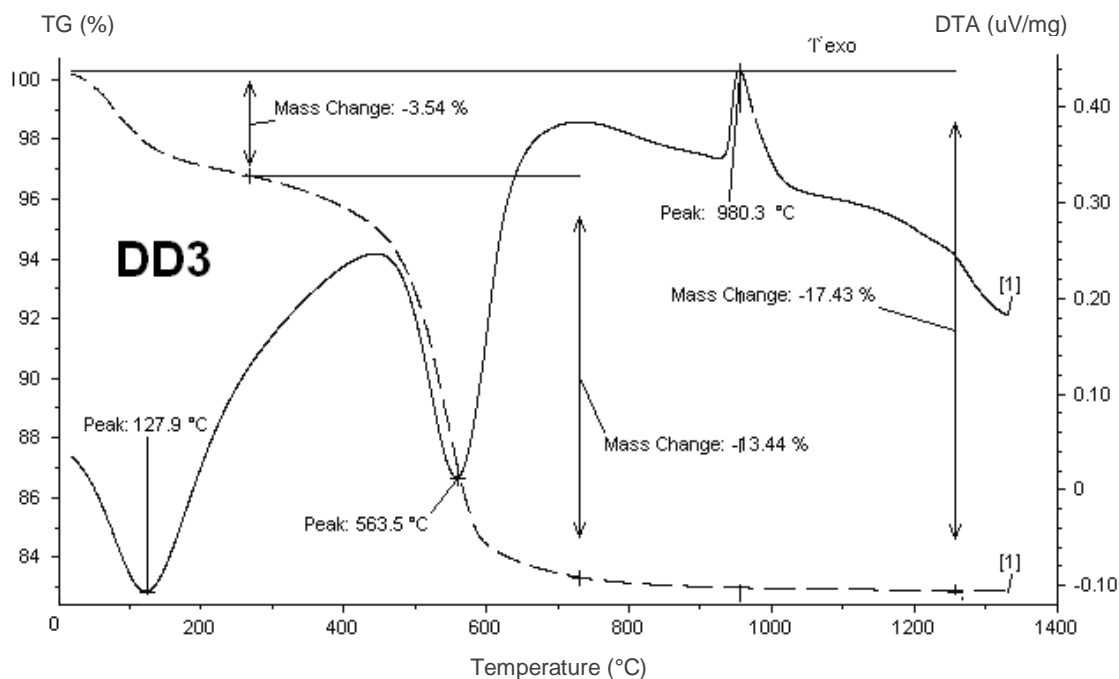**Figure 4.** Grain size distribution of DD3.

Figure 5. TG/DTA curves of the DD3 clay.

perfect structure. These changes are related to disturbances in the octahedral layer or iron can replace the aluminium until 17% weight of the mineral (Jean, 2007).

Particle size analysis of DD3 clay

Figure 4 shows the granulometric distribution of materials established by a Lazer-Granulometer of Malvern instrument - MASTERSIZER 2000.

The size analysis of the DD3 using a Laser grain size, indicates that the fractions of grains are between:

(1) 1 μm = <10%
(2) from 1 to 10 μm = 50%;
(3) from 10 to 80 μm = 40%.

Deferential thermic analysis of DD3

DTA and TG curves of DD3 clay are shown in Figure 5. Two peaks endothermic which are accompanied by two losses in weight are
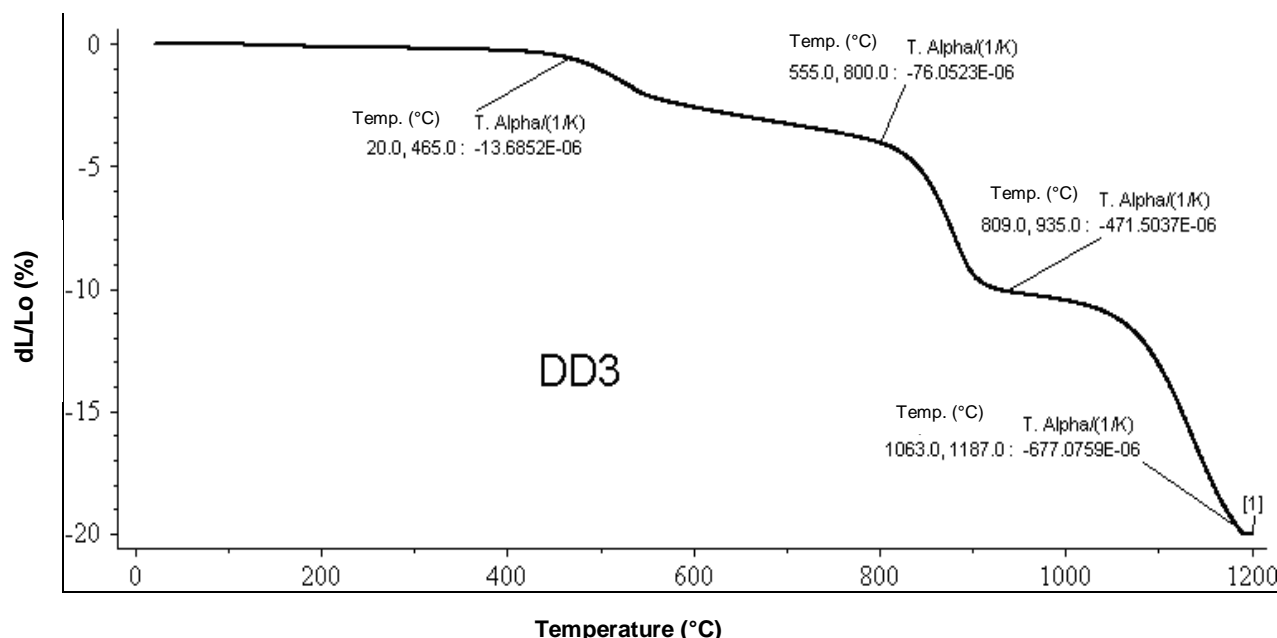
Figure 6. Dilatometer analysis of DD3 clay.

**Table 4.** Notation of variants paste and mortar.

The studied pastes	The studied mortars
P0 (reference Paste)	M0 (reference mortar)
P5 (cement + 5% DD3)	M5 (mortar + 5% DD3)
P10 (cement + 10% DD3)	M10 (mortar + 10% DD3)
P15 (cement + 15% DD3)	M15 (mortar + 15% DD3)
P20 (cement + 20% DD3)	M20 (mortar + 20% DD3)

detected, firstly at 127.9°C which corresponds to the elimination of interlayer molecules of H_2O, and second time at 563.40°C, then kaolinite undergoes its destruction by giving the metakaolin:

$$Al_2Si_2O_5(OH)_4 \longrightarrow Al_2Si_2O_7 + 2H_2O \qquad (1)$$
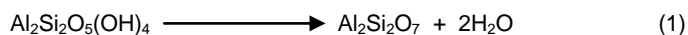
The value of this weight loss (13.44%) is very close to that of pure kaolinite (13.96%) which confirm the high tenor of kaolinite in DD3. The final weight loss totals 17.4%.

One exothermic peak is observed at 980.3°C which correspond to the temperature for mullite formation from metakaolinite as given by equation 2:

$$3(Al_2Si_2O_7) \longrightarrow Al_6Si_2O_{13} + 4SiO_2 \qquad (2)$$
Metakaolinite   Mullite   Amorphous
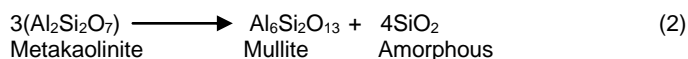
Dilatometer analysis of DD3 clay

The thermal contraction of DD3 clay is reported in Figure 6. We observe that fireclay have a classic thermal comportment of clays; (1) shrinkage between 400 and 550°C that is the dehydroxylation (equation 1), (2) shrinkage between 900 and 1000°C which corresponds to the structural reorganisation (equation 2), and shrinkage above 1000°C which corresponds to sintering. But the thermal expansion at 573°C, which characterize free silica is not observed, this may be due to the limited presence of quartz. Another observation, DD3 clay exhibits a large shrinkage >20% at 1200°C.

Procedure test

For all compositions of mortar, we have used mortars normal, according to the standard (NFP 15-403), composition:
- 450 g of cement
- 1350 g of sand
- 225 ml of water. The rate of mixing water was kept constant for all the wasted W/C = 0.5.

DD3 calcined clay has been introduced by substitution of a variable percentage of cement as 5, 10, 15 and 20%.

The experimental part aims to evaluate the influence of the addition on the mechanical and physical properties of cement. We will limit this work to the properties (normal consistency, setting time, and stability) and key properties such as mechanical (compressive and flexurel strength). In the second part we analyze the behavior of various mortars studied under two mechanisms of deterioration: damage by acid alteration and degradation due to exposure to chlorine ions. The differents compositions studied are shown in Table 4.

EXPERIMENTAL RESULTS

Thermal treatment and pozzolanic reactivity of DD3 clay

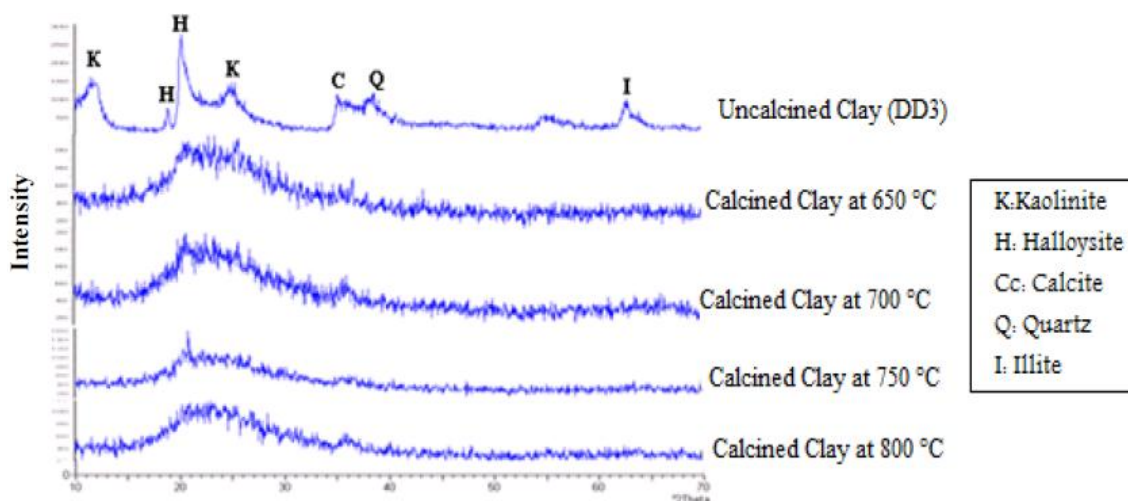For thermal treatment, DD3 clay has undergone

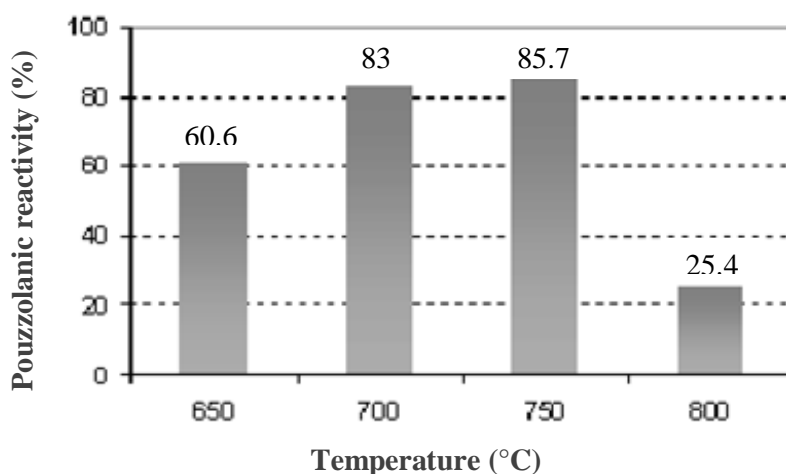**Figure 7.** Analysis by XRD of DD3 clay.

Figure 8. Evolution of the pozolanic reactivity.

calcination at different temperatures ranging from 650 to 800°C to assess its pozzolanic nature (Changling et al., 1994), and to ensure the dehydroxylation of kaolinite with transformation to metakaolin.

To assess the pozzolanic reactivity of used clay, the calcined samples was allowed to undergone analysis by X-ray diffraction. For these samples we determined the pozzolanic reactivity in a lime solution, the study of the pozzolanic reactivity of the samples was inspired by the test Chapel (Chinje and Billong, 2004; Bénoît, 1967), which is to determine the concentration difference between initial and final lime solution and allows for the rate fixed by CaO calcined clay.

The X-ray diffractograms and the results of the pozzolanic reactivity of samples calcined at different temperatures are shown in Figures 7 and 8.

According to the X-ray diffractograms obtained, there is a disappearance of the peaks of the crystalline phase for samples calcined over uncalcined clay which has fostered the emergence of the amorphous phase. The pozzolanic reactivity of the addition is indicated by the quantities of CaO determined; the results of calcined samples show a decrease in the concentration of CaO in the lime solution of at least 25.4%.

For the sample calcined at 750°C or there was a greater pozzolanic activity is the order of 85.7%. This confirms the strong pouzzolanicity of this addition. This clay after calcination allows the departure of the water content (the dehydroxylation) and the formation of metakaolin (Samet et al., 2007; Michel, 1989) with an
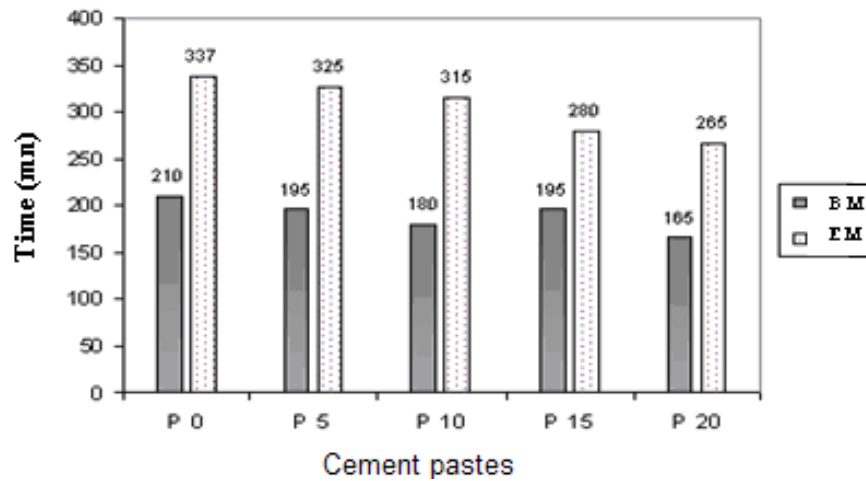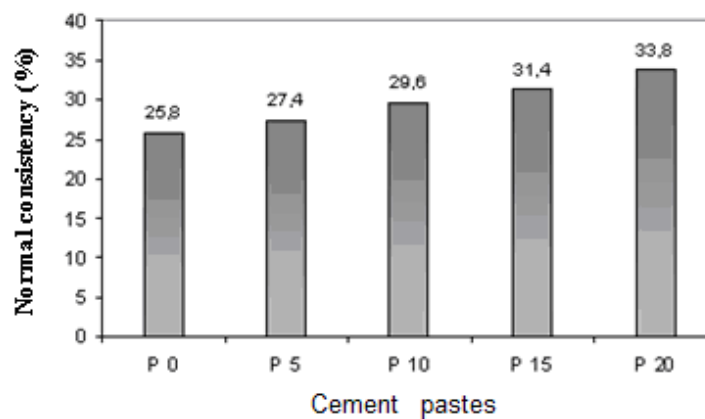
Figure 9. Time of setting pastes.

Figure 10. Normal consistency of cement pastes.

amorphous structure which makes it more reactive than the starting clay. It is an acid-base reaction. This explains the strong decrease in CaO concentration of the solution. Based on these results, we have optimized the calcination temperature to 750°C.

Physical tests of cement paste

The results of physical tests: setting time, normal consistency and expansion of different mortar compositions are summarized in Figures 9, 10 and 11.

We note a decrease of setting time according to the percentage increase added and a continuous increase of the normal consistency. This is explained by the partial substitution of cement by adding a character with clay and a high fineness (less than 80 μm), causing excessive consumption of water and absorption of one part of water for hydratation (Badogiannis et al., 2005; Bibi et al.,

2008). Given that the fixation rate of lime, responsible major part of the swelling and instability structures, increases with increasing content added there was a decrease of the opening of the needle LE Chatelier according to the increase in addition content that is less than 1 mm, therefore, better stability for high levels of addition.

Results of mortar tests

Mechanical strength of mortars conserved in water

Compressive and flexural strength are determined according to standard NF-P-15-401 and NF-P-15-400 respectively. The results of the evolution of mechanical strength test specimens of mortars, kept in water for 28 and 60 days are shown in Figures 12 and 13. The gain in compressive strength at 28 days of different compositions
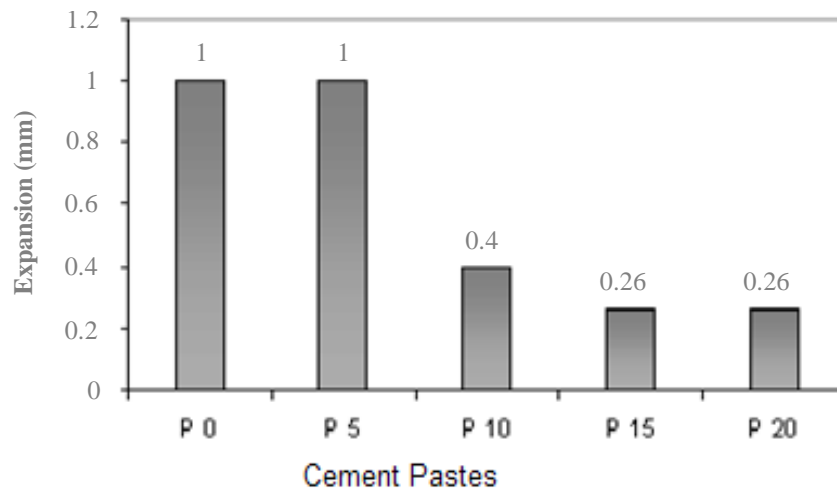
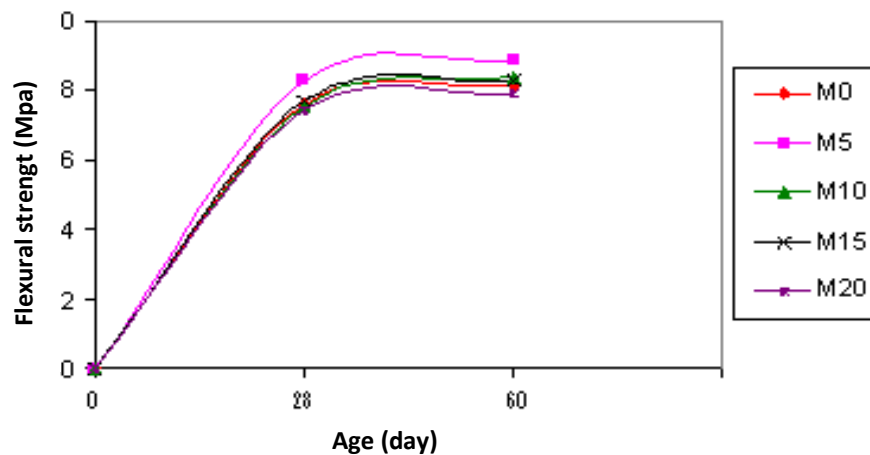**Figure 11.** Stability tests on the needles of Le Chatelier.

Figure 12. Flexural strength of the mortars at different ages.

with additions of calcined clay DD3 compared to the reference mortar is shown in Figure 14.

For all compositions of mortar, we observe a continuous increase in compressive strength and flexural strength according to age 28 and 60 days (Figures 12 and 13). This phenomenon is due to the hydration of cement causes the evolution of the compact over time. The hydration of cement constituents C_3S and C_2S, which give rise to CSH and hence increased the mechanical strength. It is also noted that the mortar of this reference resistor values was slightly higher compared with those obtained by mortars with added (M10, M20) is bending or compressive. This results in the lower constituents of cement substituted by the addition. The addition of 5% of clay burned a positive contribution to the compressive strengths of mortar, a slight improvement was identified

relative to the reference mortar (+9.88% in 28 days). Improving resistance due to formation of new CSH and CAH (Baronio and Binda, 1997), has binding properties similar to those formed based on mineral cement in the presence of calcined clay, $Ca(OH)_2$ and water.

Mass gain of mortars conserved in water

Figure 15 shows the change in weight of various mortars (M0, M5, M10, M15, M20) retained in water after 7, 14, 21, 28 and 60 days.

The beginning of curing all mortars with additions having some swelling was probably the highest finesse of the additions, which helped absorb excessive water, despite the replacement of part of cement with clay, the
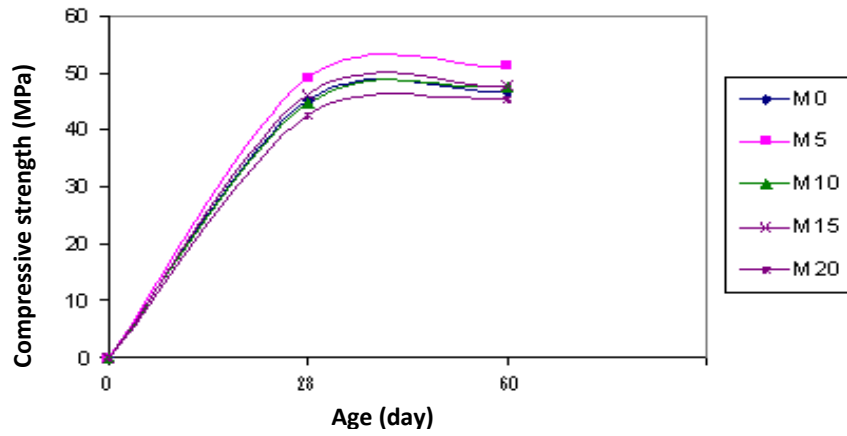
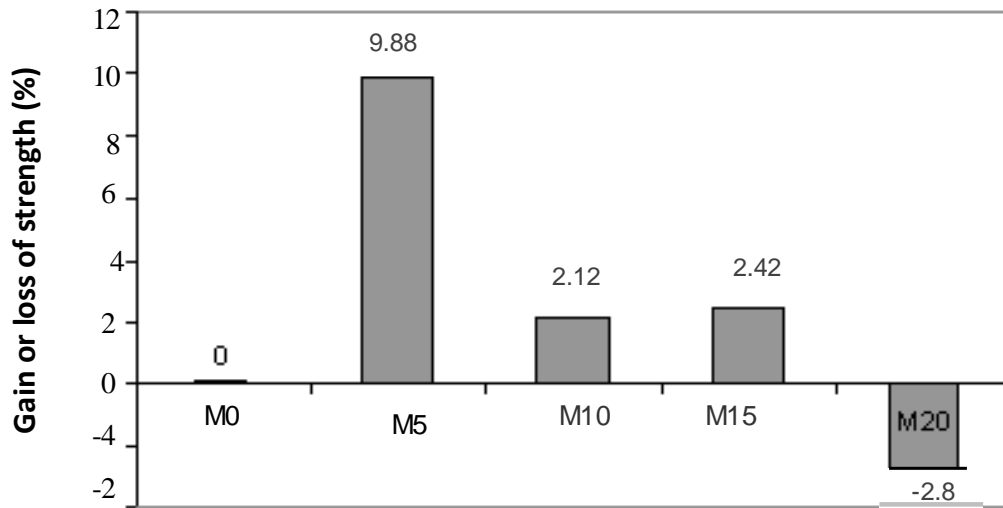**Figure 13.** Copressive strength of the mortars at different ages.

Figure 14. Gain or loss of compressive strength compared to mortars with references to 60 days.
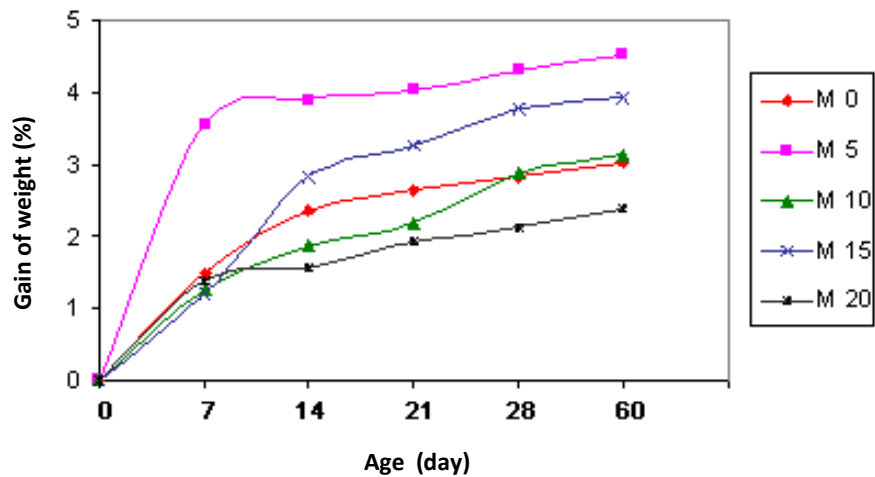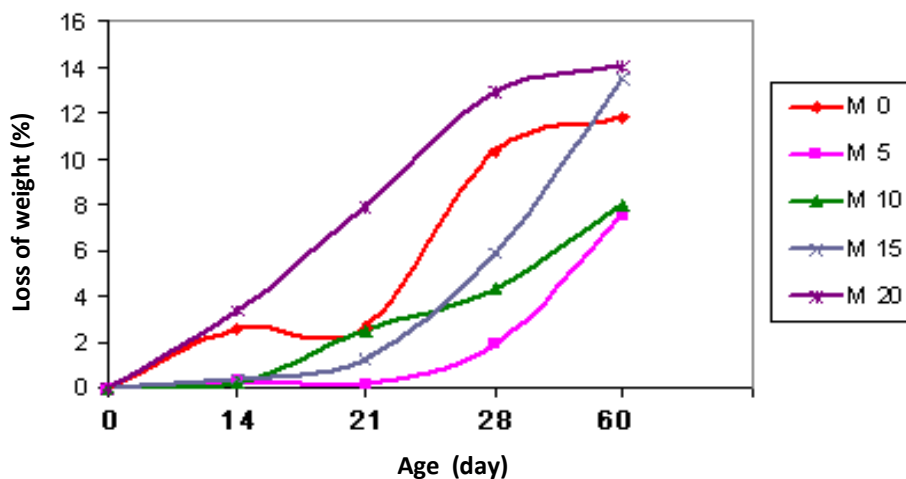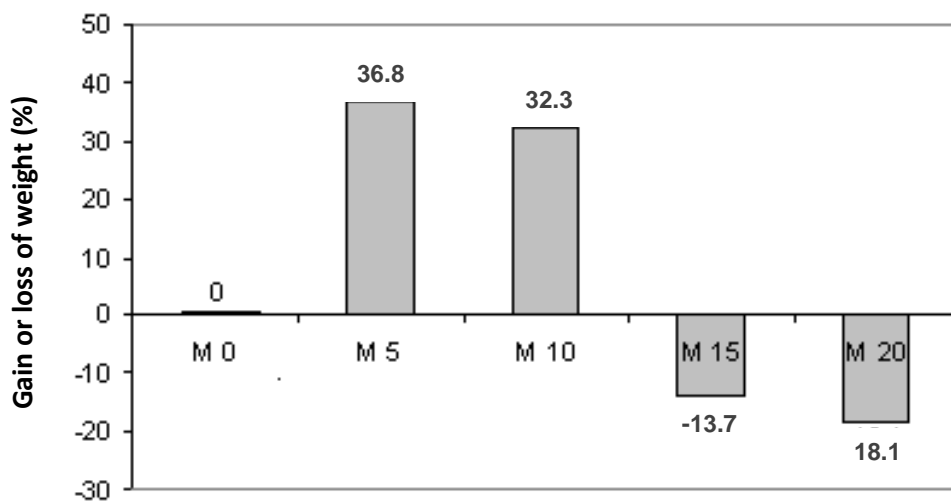

Figure 15. Gain of weight of different compositions of mortar stored in water.

Figure 16. Variation of loss weight depending on the period of immersion in the solution of H_2SO_4.

Figure 17. Gain or loss in weight of samples was based on input by adding the reference mortar after 60 days of immersion in H_2SO_4.

rate of inflation remains registered unremarkable, confirming the low influence of the addition on the phenomenon of swelling.

Study of durability

Attack by acid

To characterize the chemical resistance on acidic medium, mortars were cast into prismatic molds (4×4×16) cm³. 24 h later, samples were removed from the molds and kept in clean water. After 28 days of treatment, the samples are immersed in a solution of 5% of a strong acid sulfuric (H_2SO_4): The change in weight of specimens was examined after 14, 21, 28 and 60 days.

The chemical solution is renewed every 7 days. In the examination day, affected parts of mortar are cleanse with water, and the samples were dried for half an hour (ASTM C 267-96), and finally chemical resistant were assessed by measuring the mass loss of the specimen. Figure 16 shows the evolution of the mass loss depending on the period of immersion of various mortars stored in a sulfuric acid solution.

Figure 17 shows the gain or loss of mass based mortars additions kept for 60 days in the acidic
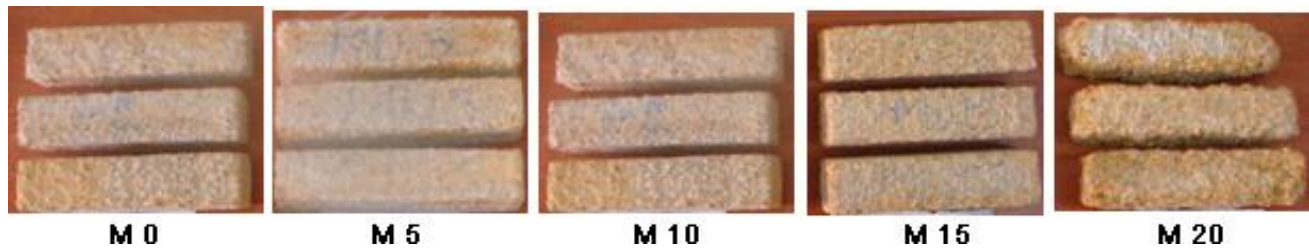
Figure 18. Specimens condition after 28 days of immersion in 5% H_2SO_4.

environment compared to the reference mortar.

Sulfuric acid (H_2SO_4) is an inorganic acid, it is more harmful to concrete and mortar than organic acid. The inorganic acids formed with $Ca(OH)_2$ content in hardened cement paste compounds are readily soluble in water.

Monitoring the mass loss of various mortars immersed in a solution of sulfuric acid (5% H_2SO_4), led us to note the continuous mass loss over time.

This loss is due to the deposition of gypsum, which is formed by the reaction between portlandite released during hydration of cement and sulfuric acid by chemical reaction:

$$Ca(OH)_2 + H_2SO_4 \rightarrow 2H_2O + CaSO_4$$
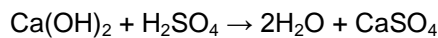
Gypsum filed forms a thick whitish coating on the surface of the mortar. Gypsum layer is easily washed and precipitate. The results are a loss of mass and a white solution. According to Figure 17, we see that the M5 and M10 mortars presents a better resistivity compared to the reference mortar with a gain of 36.8% for the M5, it is also noted that other mortar has a low mass loss.

Figure 18 shows the change in volume of various mortars after 28 days of immersion in the solution of strong acid (H_2SO_4). Visual examination of specimens shows that mortars with addition of calcined clay guard their forms after 28 days of immersion in the acid environment.

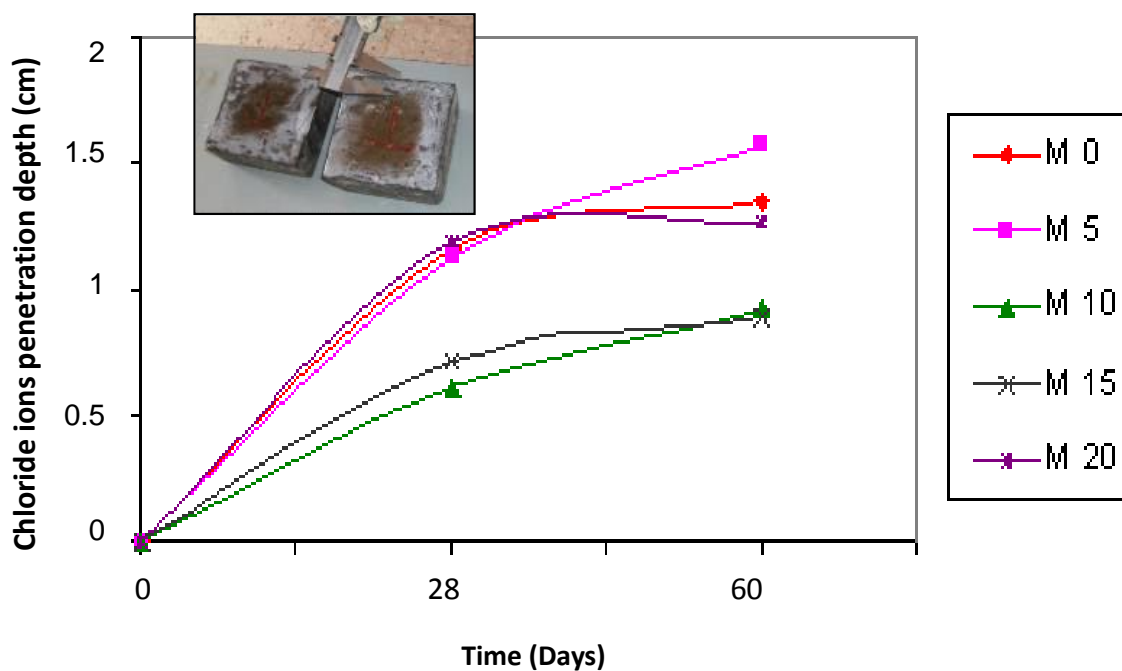**The penetration of chloride ions**

The resistance to penetration of chloride ions in mortars and concretes is one of the most important questions about the durability of concrete structures. When the chloride concentration exceeds a certain threshold, a depassivation steel occurs and there is a beginning of corrosion of reinforcing steel (Thomas, 1996; Alonso, 2000). Therefore, development of protective materials with resistance to penetration of chlorides is required for concrete structures. For this test we used cubic specimens $(10 \times 10 \times 10)$ cm^3. The mortars were made in accordance with the requirements of EN 196-1. Then the

samples are introduced into a concentrated solution of 5% NaCl, to evaluate the durability of mortars vis-à-vis the penetration of chloride ions, we followed the evolution of the depth of penetration of chloride ions at 28 and 60 days. The solutions were changed every 7 days until the age of 28 days and every 28 days until the age of 60 days. Each test specimen is divided into two parts and then solution of silver nitrate $AgNO_3$ was poured on each section according to UNI 79287 (1978). A whitish color appeared on the specimen surface, using a caliper measuring the depth of penetration of chloride ions, the results are shown in Figure 19. The test method followed in the present investigation to determine the depth of chloride penetration is reliable and accurate, and has also been recommended by other researchers (Erhan and Kasım, 2007; Wee et al., 2000; Otsuki et al., 1992; Wee et al., 1999; Meck and Sirivivatnanon, 2003).

Of various mortars, it was found that the penetration depth increases with time of immersion at 28 and 60 days for any kind of mortars and it was also recorded that variants of M10, M15 and M20 have presented a better resistance to penetration of chloride ions at 28 days compared to other alternatives (Oliveira et al., 2005). The penetration of chloride ions leads to the reaction of chloride ions with some hydrates of cement, C_3A cement is the main component of these fundamental reactions. It reacts with chloride to form calcium hydrate monochloroaluminates ($3CaO.Al_2O_3.CaCl_2.10H_2O$ or Friedel salt) or calcium hydrate trichloroaluminate ($3CaO.Al_2O_3.3CaCl_2.32H_2O$) which is subsequently its role in densifying the cement matrix by reducing the porosity of the hardened paste. Reducing the porosity of materials based on clay calcined through the formation of new compounds occupying the pores prevents the penetration of chloride ions within the mortar (Poon et al, 2006).

Application of Fick's second law of diffusion

As chloride ion penetrats through mortars in test solution with 5% NaCl concentration follows Fick's second law (Crank, 1956; Benosman et al., 2008) under nonsteady

Figure 19. Chloride ions penetration depth according to the age of immersion in test solution with 5% NaCl concentration.

state conditions for diffusion, the solution to the law is given by the following equation:

$$\frac{C}{C_0} = 1 - erf\left(\frac{x}{2\sqrt{Dt}}\right) \qquad (3)$$

Where C is the concentration of chloride ions at a chloride ion penetration depth, x is distance from the penetration dept, C_0 is the concentration of chloride ions at the exposed surfaces, t is the immersion period in the NaCl test solutions, D is chloride ion diffusion coefficient, and erf is error function available in standard mathematical tables. An approximation to equation (3) is expressed as follow (Benosman et al., 2008):

$$x = 4\sqrt{Dt} \qquad (4)$$

Generally the chloride ion penetration depth of mortar increases with additional immersion period. As seen in Figures 20 (a, b, c, d, e) the plots $xf(\sqrt{t})$ are approximatively linear and the plots follow Fick's second law.

The apparent chloride ion diffusion coefficient was obtained from the slopes of $x-(\sqrt{t})$ lines after the fitting of experimental data of the profiles type to equation (4), in The apparent chloride ion diffusion coefficient of the

mortar as illustrated in this figure show that mortars with 5, 10, and 20% of calcined clay presents a chloride ion diffusion coefficient much smaller than that of mortar without addition.

The hydration of cement led to the formation of new hydrates (C-S-H gel) in time in presence of calcined clay. Its makes the cementing matrix denser and reduces the porosity of mortar, which reduces the penetration of chlorides ions.

Conclusion

All previous results show unequivocally that the presence of the substituent, DD3 clay calcined at 750°C in the cement matrix affects the mechanical and physical properties of mortar on the one hand and their behavior to chemical attack in the other hand: Mortars based on clay presents a very good stability against swelling. The study of mechanical performance showed the maintining of strength, and in some conditions improving.

The largest gain was obtained for a substitution rate of 10% with 9.88 to 60 days for the M15 and M20 the fall was not remarkable. The addition of calcined clay as cement replacing has a beneficial effect on durability, because adding mineral contributes to the densification of the hardened cement paste through the consumption of portlandite by forming CSH and CAH, which increases the impermeability of cement matrix.
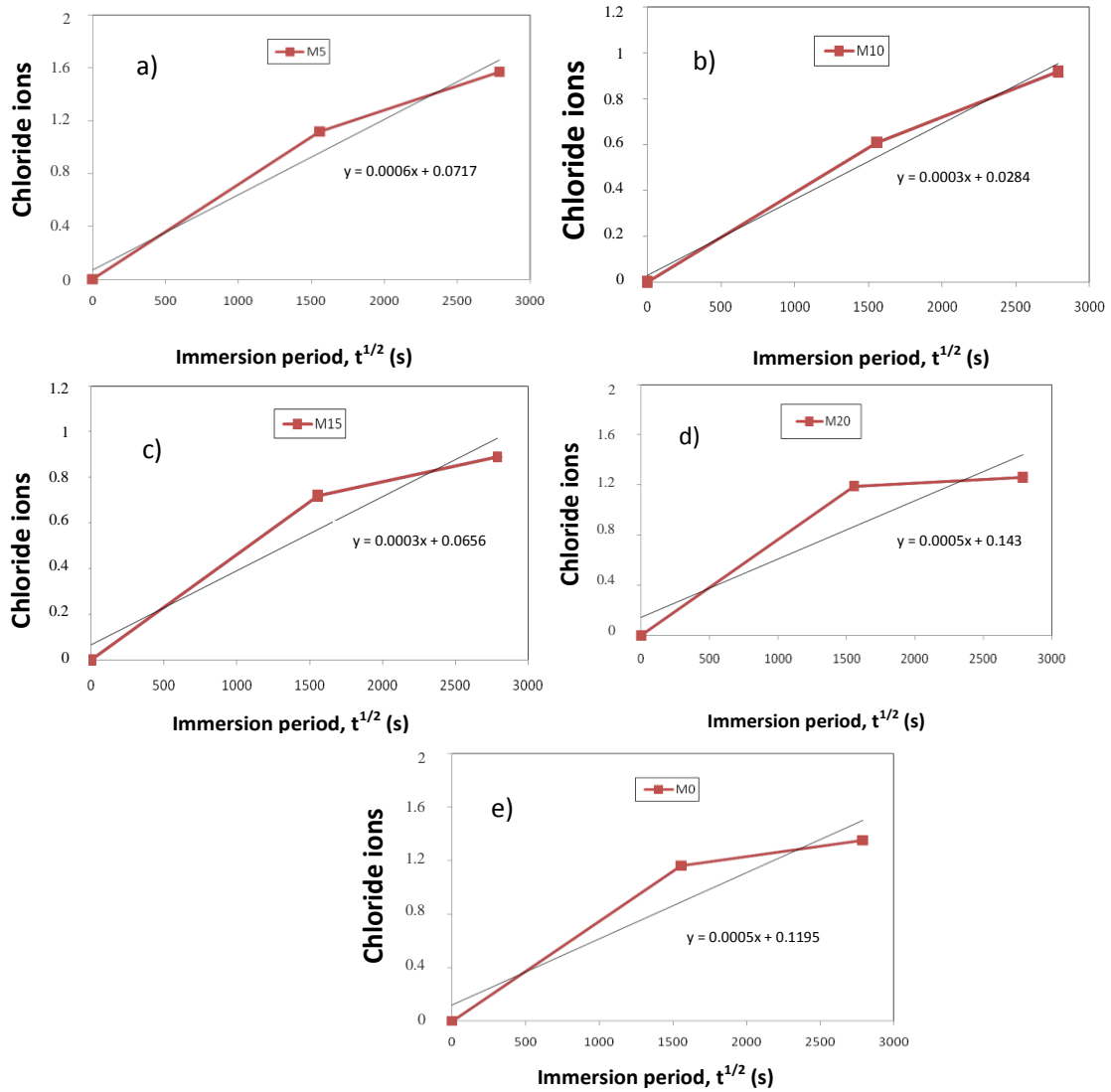
Figure 20. Immersion period versus chloride ion penetration depth of mortars in 5% NaCl immersion.
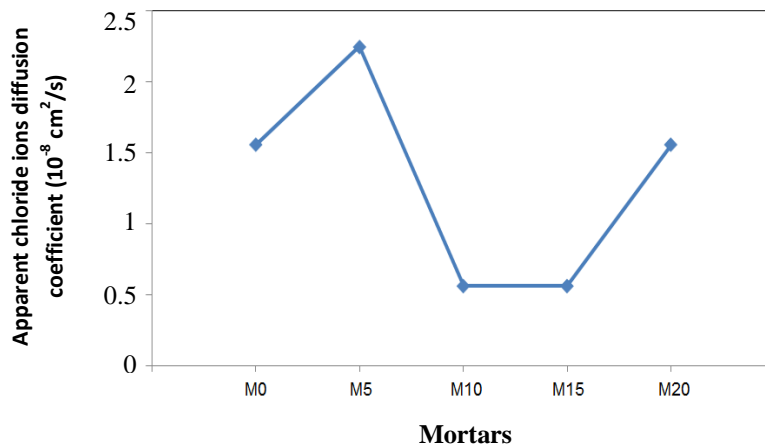

Figure 21. Apparent chloride ion diffusion coefficient of mortars.

The M5 and M10 mortars presents better resistivity compared to the reference mortar with a gain of 36.8% for the M5.

The addition of calcined clay reduced the penetration of chloride ions in the mortars, and increases resistance in acidic media. By varying the percentage of calcined clay DD3, we could get based on fields of use, different type of cements with the mechanical and physical properties required.

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