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# Formulation and characterization of a new ecological cementitious material at base of different percentage of limestone fillers: Study of physical-chemical and mechanical properties

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#### Abstract

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#### Keywords

- ✓ Formulation,
- ✓ Cementitious Material,
- ✓ Limestone fillers,
- ✓ Porosity,
- ✓ Capillary Absorption,
- ✓ Physical Properties,
- Durability,
- Compressive Strength.

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#### 1. Introduction

which occurs during the production of cement and to improve the physical properties and mechanical performance of mortars and/or concrete, we have incorporated a mineral addition which is the limestone fillers (F-Lime) in their formulation matrix. While partially substituting the clinker by this one at various percentages ranging from 5% to 40% by weight of cement with a step of 5% in presence of a superplasticizer. The influence of the incorporation of F-Lime on the physical properties (fineness by specific surface Blaine /density/setting of initial and final time/water content) was studied on one hand. The effect of the addition of F-Lime on the mechanical performance (compressive strength/porosity/capillary absorption) was evaluated on the other hand. The obtained results by different formulations prospected showed that the addition of F-Lime in the formulation matrix of a cementitious material increases the fineness. Moreover, its density was decreased. We observed that the setting time increases with the percentage of F-Lime was increased. Similarly, the compressive strengths at a young age (2 days), median age (7 days) and long-term (28 days) were improved. The W/C report, the porosity, and the capillary absorption have been decreased. These results show that we have succeeded to produce an ecological and durable cementitious material.

To contribute the minimization of emissions of greenhouse gas (GHG) into the atmosphere

The use of organic and inorganic additions in the manufacture of cement contributes to minimizing the emissions of greenhouse gasses into the atmosphere, notably the carbon dioxide (CO<sub>2</sub>) [1, 2]. The cement industry is responsible for approximately of 7% of these gasses from the decarbonisation of limestone, which results in the release of carbon dioxide into the atmosphere, according to the following chemical reaction: CaCO<sub>3</sub>  $\rightarrow$  CaO + CO<sub>2</sub> [3, 4]. This reaction represents for more than 60% of emissions of CO<sub>2</sub> from the cement manufacturing and the leftovers are due to the transportation, the energy needs of the process of clinkerisation (fuel) and grinding [4 - 7].

The use of limestone fillers (F-Lime) as an addition in the manufacture of cement and various types of concretes will reduce the energy, raw materials consumption and minimize the emissions of carbon dioxide into the atmosphere [7, 8]. The incorporation of these additions will also cause a change in granular distribution [9 - 14], this engenders in a modification of some physical properties in the fresh state, namely the setting time, the water content on one hand [11 - 15], and in hardened states, such as the porosity, the capillary absorption, and the evolution of compressive resistance on the other hand [15 - 21].

In this experimental different formulation of cementitious materials were developed all by partially substituting the clinker by the limestone fillers at different percentages ranging from 5% to 40% by weight of cement with the step of 5%. The influence of the incorporation of limestone fillers on the physical properties of fresh cement paste has been studied on one hand. And the effect of the introduction of these fillers on the mechanical performance at hardened State, namely the porosity, the capillary absorption, and the compressive strength was evaluated on the other. In order to improve the physical properties in the fresh state (reduce the water demand) and the mechanical performance in hardened State (porosity, capillary absorption, and the compressive strength), a superplasticizer nature of high water reducer and the accelerator setting were used .

The results of different formulations show that the partial substitution of clinker by the limestone fillers reduces the amount of water used. Similarly, the introduction of these fillers in the formulation matrix causes positive effects on mechanical performance of concrete.

### 2. Experimental details

#### 2.1. Materials

#### 2.1.1. Cement

The type of cement used in this work is (CMI-42.5). This a Portland cement as a resulting from simultaneous at (95%) of clinker and (5%) of gypsum accordance to the standard EN 196-1. It is from of a cement factory of Amran - Yemen. The chemical compositions (clinker, gypsum, and cement) and mineralogical (clinker) determined by X-rays fluorescence (XRF) are presented in the tables (1 and 2).

Chemical name	Chemical formula	Cement nomenclature	Clinker	Gypsum	Cement
Lime	CaO	С	62.76	33.40	61.29
Silica	SiO <sub>2</sub>	S	21.00	0.70	19.99
Alumina	$Al_2O_3$	А	5.84	0.36	5.57
Ferrite	$Fe_2O_3$	F	3.00	0.09	2.85
Magnesia	MgO	М	1.96	0.63	1.89
Sulfur trioxide	$SO_3$	Ś	0.90	47.20	3.22
Potassium oxide	K <sub>2</sub> O	K	1.21	0.03	1.15
Sodium oxide	Na <sub>2</sub> O	Ν	0.20	0.10	0.20
Chloride ion	Cl	Cl	0.02	0.01	0.02

Table 1:Elementary chemical compositions of clinker, gypsum and cement in weight of atomic

Table 2:Mineralogical composition of clinker											
Chemical name	Mineral name	Chemical formula	Cement nomenclature	Content							
Tricalcium silicate	Alite	Ca <sub>3</sub> SiO <sub>5</sub>	$C_3S$	47.70							
Dicalcium silicate	Balite	$Ca_2SiO_4$	$C_2S$	25.10							
Aluminate tricalcium	Aluminate	$Ca_3Al_2O_6$	C <sub>3</sub> A	10.40							
Tetracalcium Aluminoferrite	Ferrite	$Ca_4Al_2Fe_2O_{10}$	$C_4AF$	9.10							

The physical and mechanical characteristics of cement are presented in table (3).

Designations	Values	Units
Absolute Density	3240.00	g.cm <sup>-3</sup>
Refusal of the sieve 45 µm	12.50	%
Refusal of the sieve 90 μm	1.50	%
Specific surface Blaine	3.14	$cm^{2}g^{-1}$

# Table 3. Physical properties of cament used

#### 2.1.2. **Limestone** Fillers

They are mineral materials which spread in several regions in Yemen, such as Hadramaout, Sana'a, Amran and etc. (Figure 1) [22]. These materials occupy a volume about of 3.6 billion m<sup>3</sup>. They are obtained by grinding limestone rock, they have a physical-chemical effect and a granulated effect, and they accelerate of hydration of cement. In general, they have a light color, making them suitable for obtaining good quality siding.



Figure 1: Deposit of extract the pure limestone in Bani Qais-Amran-Yemen

The results of the analysis by X-ray fluorescence (XRF) of limestone fillers of Bani Qais-Amran - Yemen after crushing, drying in the oven and grinding are represented in the table (4).

Table 4: Elementary chemical compositions of innestone inners in weight of atomic												
CaO	SiO <sub>2</sub>	$Al_2O_3$	Fe <sub>2</sub> O <sub>3</sub>	MgO	$SO_3$	K <sub>2</sub> O	Na <sub>2</sub> O	Cl	LOI			
54.96	0.62	0.12	0.16	0.41	0.08	0.01	0.00	0.00	43.63			

Table 4: Elementary chemical compositions of limestone fillers in weight of atomic

From the results shown in the table (4), we observed that the limestone fillers of Bani Qais-Amran-Yemen contained 54.96% of Lime (CaO) / 0.62% of Silica (SiO<sub>2</sub>) / 0.12 of alumina (Al<sub>2</sub>O<sub>3</sub>)/ 0.16 iron of (Fe<sub>2</sub>O<sub>3</sub>). The sum of the percentages is equal to 56.36% and the remainder represents the loss on ignition (LOI), which presents the water and CO<sub>2</sub>. These limestone fillers have a specific surface Blaine 4776 cm<sup>2</sup>.g<sup>-1</sup> and a density 2.13 g.cm<sup>-3</sup>. The results of the mineralogical analysis by X-rays diffraction of (XRD) of limestone fillers of Bani Qais-Amran - Yemen are represented in figure (2).



Figure 2: Spectrum of limestone fillers

From the figure (2), we noticed that the limestone fillers reveal the strong presence of calcite (CaCO<sub>3</sub>), followed by Dolomite (CaCO<sub>3</sub>/MgCO<sub>3</sub>), then of carbonate of magnesium (MgCO<sub>3</sub>) and magnesium hydroxide Ca(OH)<sub>2</sub> / Mg(OH)<sub>2</sub>. The result of the analysis by metallography microscope of this addition gives an indication of the rearrangement of particles of a composite powder state is shown in figure (3).



Figure 3: View by metallography microscopic at 100x (a) and (b) 200x of limestone fillers

The particles of limestone filler are shown in the form of rosettes. They are displayed in figure (3 'a' and 'b') using the two enlargement metallography microscopic (100x and 200x).

### 2.1.3. High Range Water Reducing And Accelerating Superplasticizer

High Range Water Reducing and Accelerating Superplasticizer (HRWRASP103) are liquid-form polymers specially synthesized for the concrete industry. They are based on sodium or calcium salts of sulfonated polynaphthalene (figure 4) or sodium salt of sulfonated poly-melamine [EN 934-2] (figure 5). The physical properties of High Range Water Reducing and Accelerating superplasticizer (HRWRASP103) gathered at the table (5).





melamine

<b>Table 5:</b> Physical properties of superplasti
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Name	Nature	Color	Density ( $g \text{ cm}^{-3}$ )	Area training (%)	Chloride content
I tulle	i tutui e	D			
HRWRASP103	Liquid	Brown	1.20	0.50 - 1.00	Nil

#### 2.1.4. Water

The water used to mix the mortar and/or concrete is tap water. The main characteristics of these waters are summarized in table (6).

Components	Units	Values
pH	-	7.00
Turbidity	(mg/L)	450.00
$CO_{3}^{-2}$	(mg/L)	216.00
HCO <sub>3</sub>	(mg/L)	0.00
$Ca^{+2}$	(mg/L)	56.40
$Mg^{+2}$	(mg/L)	52.40
Conductivity	μS/cm	692.00

Table 6:	Main	features	of the	mixing	water
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#### 2.1.5. Sand

To make our mortar, we used standard sand according to the norm EN 196-1, delivered by the new French company of Littoral. Its particle size analysis is illustrated in figure (6).



Figure 6: Granulometric curve of sand

The particle size analysis presented in figure (6) shows that used sand grains are distributed in a systematic way according to the specifications of the standard EN 196-1.

#### 2.2. Methods

### 2.2.1. The density

The density of cement is measured by the displacement of an inert liquid with respect to the cement inside a graduated vessel. It is measured using a "Le Chatelier" apparatus according to the specification of the norm EN 196-6 / ASTM C188 / NM 10.1.004. We have determined the absolute density of cement from two measurements as follows:

- The first measure is to fill the volumenometer"Le Chatelier" with a liquid until the level of the liquid reaches between the graduations and tonote this level the initial level: V<sub>0</sub>.
- The second measure is to introduce the mass of cement with the aid of the spatula, avoiding leaving the cement to settle on the walls. Then, we recording the mass of the cement: m, when all the cement introduced, we incline Le Chatelierat 45° with respect the work plan, by following, roll the volumenometer by a reciprocating motion to expel the air; Finally, the let it rest vertically. Then, we note the final level V<sub>1</sub>. The absolute density of cement is calculated using equation (1). It is expressed in g.cm<sup>-3</sup>.

$$\rho = \frac{m}{V_1 - V_0}; \frac{g}{cm^3}$$

Equation (1)

Where:

 $\rho$  :The density of cement in g.cm<sup>-3</sup>; m: The mass of cement in grams; V<sub>0</sub>: The volume of the initial level in cm<sup>3</sup>;

 $V_0$ . The volume of the final level in cm<sup>3</sup>.

#### 2.2.2. The fineness by the method of air permeability (method of the specific surface Blaine)

It is the total surface area of the grains contained in a powder mass [23 - 25]. The Fineness by the air permeability method is measured using the Blaine apparatus according to standard 10.1.005 NM. After we have determined the density the sample of cement using the Le Chatuler apparatus, we weighed an amount of cement  $(m_1)$  to obtain a cement bed formation with porosity: e = 0.500 and  $m_1 = 0.500 \times \rho \times V$ .

With:  $\rho$ : The density of cement in (g.cm<sup>-3</sup>);

V: The volume of cement bed in  $(cm^3)$ .

Subsequently, we placed the perforated metal disk on the shoulder at the bottom of the cell and placed on this metal disc a disc of filter paper. Then we made sure that the filter paper disc completely covers the perforated metal disc and that it is flat. Then we placed the weight of cement quantity,  $m_1$ , into the cell taking care to avoid any loss of material. Subsequently, we tapped the cell to level cement and placed a second disc of filter paper blank on leveled cement. Afterwards, we inserted the plunger until the lower face of its shoulder comes into contact with the cell. And finally, we slowly removed the plunger about 5 mm, rotated 90 ° and exerted a new delicate but firm pressure on the bed until the shoulder of the plunger came into contact with the cell.

The mass area "S" is calculated by the equation (2) and expressed in 
$$\text{cm}^2.\text{g}^{-1}$$
.

$$S = \frac{\kappa}{\rho} \times \frac{\sqrt{e^3}}{1 - e} \times \frac{\sqrt{t}}{\sqrt{0.1\eta}}; Cm^2/g$$
 Equation 1

### 2.2.3. Method of preparation of fresh cement paste

The experimental protocols used to determine the physical properties of fresh cement paste, namely the standard consistency (W/C report) and the initial and final time are given in the standard EN 196-3. This is to make a paste of cement with 500 g of cement with the limestone fillers into the bowl of the mixer. The amount of water needed is chosen taking into account on the different percentages of the limestone fillers used in our formulations that show in table (7).

Content		DT	P.F-Lime							
		PI	5%	10%	15%	20%	25%	30%	35%	40%
Comont	Mass (g)	500	475	450	425	400	375	350	325	300
Cement	%	100	95	90	85	80	75	70	65	60
F-Lime	Mass (g)	0	25	50	75	100	125	150	175	200
	%	0	5	10	15	20	25	30	35	40
Water	Mass (g)	140	143	146	148	150	153	155	157	160
	%	0.280	0.286	0.292	0.296	0.300	0.306	0.310	0.314	0.320

Table 7: Formulation matrix of cement paste with different percentages of F-Lime

We immediately put the mixer with a slow speed for 90 Sec. Then we stopped the mixer for 15 Sec to bring the paste which is located beyond the mixing zone. Subsequently, we restarted the mixer at slow speed for 90 Sec. After we quickly introduced the paste into the frustoconical mold placed on a glass plate, without excessive compaction or vibration. Then the assembly is placed on the plate of the Vicat apparatus. Afterwards, we

measured the separation distance between the end of the probe and the base plate. This distance (d) is the consistency of the paste studied (W/C report). And finally the paste of cement with a standardized consistency will be placed on the plate of the Vicat automatic device to measure the initial and final time.

#### 2.2.4. Methods of preparation of mortar and/or concrete in the hardened State

To achieve the objective of our study, we prepared a mortar of reference without and with limestone filler and superplasticizers which the compositions are inspired by the normal mortar defined by the standard EN 196-1, with a quantity of water and adjusted and a paste with a consistency standard as shown in the table (8). The procedures followed for the preparation of our mortars begin with mixing, the procedures followed for the preparation of our mortars begin with mortar twice and by applying to the mold 60 shocks each time using the shock device. After the mold is leveled, covered with a plate of glass and stored in the wet room. After 20 h or 24 h from the start of the mixing, the specimens are removed from the mold and stored in water at 20 ° C  $\pm$  1 ° C until the time of test of rupture. The compressive strengths were measured at a young age (2 days) in median age (7 days) and long-term (28 days) using a bending test machine (figure 7) to break the specimen into two halves and each party is responsible the subject of compressive using a hydraulic compressive testing machine (figure 8) [1]. The value of the resistance is considered as the average of the crushing stress of three test pieces (6 halves).



Figure 7: Device of bending load for the mortar specimens



Figure 8: Device in compressive load for the mortar specimens

The compressive strength was calculated using the equation (3).

Compressive strength = 
$$\frac{\text{Load ,in "N"}}{\text{Area, in "mm^2"}}$$
; MPa

Equation 2

Content		МТ	M.F-Lime							
		IVI-1	5%	10%	15%	20%	25%	30%	35%	40%
Comont	Mass (g)	450	427,5	405	382,5	360	337,5	315	292,5	270
Cement	%	100	95	90	85	80	75	70	65	60
E Lima	Mass (g)	0	25	50	75	100	125	150	175	200
F-Lime	%	0	5	10	15	20	25	30	35	40
Sable	Mass (g)	1350	1350	1350	1350	1350	1350	1350	1350	1350
Watan	Mass (g)	225	227	231	233	235	238	239	241	243
Water	%	0.500	0.504	0.513	0.518	0.522	0.529	0.531	0.536	0.540

Table 8: Formulation matrix of mortar and/or concrete with different percentages of F-Lime

### 2.2.5. Porosity

The porosity is an essential feature of the mortar or concrete at hardened State [27]. It is a part of the factors that determine the durability of concrete. It is obviously calculated using the equation (4).

$$P = \frac{V_P}{V_T}$$

With:

V<sub>P</sub>: The pore volume of the specimens;

 $V_T$ : The total volume of the specimens, that is to say, the sum of the volume of solid and the volume of the pores.

Equation 3

### 2.2.6. Capillary absorption

The capillary absorption (CA) of our formulations at different percentages of F-Lime was calculated by using the equation (5). It is expressed in g.mm<sup>-2</sup>.

$$CA = \frac{M_f - M_i}{S}$$

Equation 4

With:

CA: The capillary absorption (g.mm<sup>-2</sup>)

M<sub>f</sub>: The mass of the specimen after conservation for 2 days, 7 days and 28 days, in grams;

M<sub>i</sub>: The mass of the specimen before conservation under the water in grams;

S: The area of the specimens in (mm).

### 2.2.7. Gain of compressive strength at 28 days

We calculated the gain of compressive strength at 28 days using equation (6), it is expressed in percentage.

$$G = \frac{R_{mcx} - R_{mct}}{R_{mct}} x100$$
 Equation 5

Where:

R<sub>mct</sub>: Control of compressive strength of mortar at 28 days;

 $R_{mcx}$ : Compressive strength of mortars with F-Lime and 2.5 % of superplasticizerand X = 5%, 0% ...... 40%.

### 3. Results and discussion

#### 3.1. Effect of addition of limestone fillers on the physical chemical properties

The table (9) presents the physical-chemical properties of cement at the base of different percentages of limestone fillers.

Tuble 7.1 hysical chemical properties of cement at base of anterent percentages of intestone mens										
Contant		МТ	5%-F-	10%-F-	15%-F-	20%-F-	25%-	30%-	35%-	40%-
Content		IVI I	Lime	Lime	Lime	Lime	F-Lime	F-Lime	F-Lime	F-Lime
Density "g.cm <sup>-3</sup>	· · ·	3.14	3.13	3.12	3.10	3.09	3.08	3.07	3.05	3.02
Fineness by surface"cm <sup>2</sup> .g <sup>-1</sup> "	specific	3240	3315	3400	3570	3610	3690	3810	3920	4050
Setting	Initial	60	60	60	55	55	50	50	40	40
time"min"	Final	90	110	110	105	100	100	90	90	80
W/C	F-Lime	0.50	0.50	0.51	0.52	0.52	0.53	0.53	0.54	0.54

Table 9: Physical-chemical properties of cement at base of different percentages of limestone fillers

From the results shown in the table (9), we observed that the density of the new binder at a base of F-Lime was decreased in comparison with cement control "MT". For example the addition of 40% of F- Lime in the cement formulation matrix decreases the density from  $3.14 \text{ g.cm}^{-3}$ to  $3.02 \text{ g.cm}^{-3}$ . This decrease is logically explained by the fact that the limestone fillers have a real density lower than cement [28]. We also noticed that the finesse by air permeability increases with the addition of F-Lime. This increase is usually due to the fineness of F-Lime. We found that the ratio of W/C of our new cementitious material at the base of F-Lime increases with the mass fraction of this. This is usually due to the chemical and mineralogical composition of our addition that is rich in CaO; the presence of high rate in calcium oxide has an influence on the hydration phenomenon, as a limestone rich in this mineral phase tends to have a high water demand. More, the presence of the limestone fillers in the mix acts favorably the physical properties of a cementitious material, namely, the initial and the final time. These have been reduced considerably depending on the percentage of F-Lime, which gave to our materials the role of a setting accelerator. This reduction in the setting time is due generally to the chemical and mineralogical compositions of our add compound which are rich in CaO and poor in Al<sub>2</sub>O<sub>3</sub> on one hand, and on the other hand it is owing to them fineness of that fills the voids between the cement particles, which thereafter improves the porosity of concrete and their compressive strength.

### 3.2. Influence of add of F-Lime on mechanical performance of mortar and /or concrete

The figure (9) exposes the variation of the compressive strength of the cementitious material at the base of F-Lime as a function of time in days.



Figure 9: The compressive strength of cementation material as a function of time in days

From the figure (9), we noticed that the compressive strength of all mortars at a base of F-Lime is steadily increasing with age and does not fall. However, its resistance decreases considerably with the increase of adding F-Lime. To better improve the physical properties (the ratio of W/C, the porosity and the capillary absorption) and mechanical performance [25 - 27], we have incorporated a high range water reducing and accelerating superplasticizer by a rate of 2.5% by weight of cement in the formulation matrix of cementitious material at base of F-Lime.

3.3. The effect of the addition of F-Lime with superplasticizer on the quantity of mixing water (report of W/C) To determine the optimal amount of mixing water of each test, we have maintained in all our experiences the standard consistency fixed, it varies between 5-7 mm according to the specification of the standard (NF EN 196-3) + A1. This experiment was performed using the apparatus Vicat according to the standard (NF EN 197-1). The figures (10 and 11) show the variation of a report of W/C and the percentage of water reduced as a function of the mass fraction of F-Lime with superplasticizer.



Figure 10: The report of W/C as a function of the mass fraction of F-Lime with superplasticizers

According to the figures (10 and 11), we found that the introduction of superplasticizers in the formulations of cementitious material at the base of different percentages of F-Lime reduces the amount of water used and therefore the ratio of W/C has been decreased. This reduction in the quantity of water and the ratio of W/C is generally due to the action of the dispersion exerted by the superplasticizer on the solid surface (cement). This subsequently promotes their dispersion due to a phenomenon of steric congestion [29, 30].



Figure 11: Theamount of water reduced as a function of mass fraction of F-Lime with superplasticizer

### 3.4. The influence of addition of F-Lime with superplasticizers on durability

The concrete is a porous material [31, 32]. Therefore, low porosity and capillary absorption constitute the best defense against the concrete aggressive agents.

#### > Porosity

The figure (12) illustrates the evolution of the porosity as a function of the mass fraction of F-Lime with the superplasticizer.



Figure 12: The porosity of cementation material as a function of mass fraction of F-Lime with superplasticizers

From the figure (12), we observed that the porosity decreases as a function of the addition of F-Lime were increased in the formulation matrix. This decrease is due logically to the fact that the molecule of superplasticizer favors the dispersion of grains of cement on one hand and on the other hand that the fillers of limestone fillers fill the interstitial voids between the grains of cement and sands which decreases the pores inside the material and improve the mechanical performance.

### ➤ Capillary absorption

The figure (13) presents the developments in capillary absorption based on the mass fraction of F-Lime with superplasticizer. The figure (13) shows that the capillary absorption of the mortars has been influenced by the pore structure and the rate of the superplasticizer. The last one can be contributed to the reduction of capillary absorption by the formation of a polymeric film and reduction of capillary pressure.

### 3.5. Influence of addition of F-Lime with superplasticizer on mechanical performance

The figure (14) presents the evolution of mechanical of compressive strength of the cementitious material at different percentages of F-Lime with superplasticizer as a function of time.



Figure 13: The capillary absorption of cementation material as a function of the percentage of F-Lime with superplasticizers



Figure 14: The compressive strength of cementation material as a function of time in days with superplasticizers

From the figure (14), we found that the compressive strengths at a young age (2 days), median (7 days) and long-term (28 days) increases with the addition of F-Lime and superplasticizer increases. These increases can be explained by the fact that the incorporation of superplasticizer into the formulation matrix manifests itself by dispersing the grains of binders, which facilitates the hydration of the mixture during the mixing on one hand and to improve its porosity on the other hand.

The figure (15) shows the results of analysis by the metallography microscope of cementitious material at different percentages of F-Lime (from 5% to 40% by weight of cement) with superplasticizer. According to the results obtained by metallography microscopy of different formulations of cementitious material (figure 15), we have noted that the fillers of limestone by their fineness have filled the voids that exist between the particles of cement and that of sand aggregates. In other words, the addition of limestone fillers in the formulation of cementitious material has a granular effect, which decreases the porosity and thereafter increases the compressive strength.

The figure (16) shows the results of the analysis by the XRD of different formulations of cementitious material at the base of different percentages of F-Lime (from 5% to 40% by weight of cement) with superplasticizer. From, the figure (16) shows that the limestone fillers by their high lime levels increase the calcite phase. This last one has been consumed by the silica present in the mixture, which reduces the porosity in the present of superplasticizer, reduces the amount of water used "aggregate effect" and increases the compressive strength at a young age (2 days), median age (7 days) and long-term (28 days) (figure 14), "physical-chemical and chemical effects".



Portland cement



Mortar at base of 15 % of F-Lime



Mortar at base of 30 % of F-Lime



Mortar at base of 5 % of F-Lime



Mortar at base of 20 % of F-Lime



Mortar at base of 35 % of F-Lime



Mortar at base of 10% of F-Lime



Mortar at base of 25 % of F-Lime



Mortar at base of 40 % of F-Lime

Figure 15: View by metallography microscopic of different formulations of the cementitious material as a function of the mass fraction of F-Lime with superplasticizers



Figure 16: Spectrum of XRD analysis of different formulations of cementations material as a function of the mass fraction of F-Lime with superplasticizers

Also, we have calculated the compressive strength at 28 days of different formulations based off different percentages of F-Lime ranging from 5% to 40% with and without superplasticizers.

The figure (17) shows the variation of the compressive strength of the cementitious material at 28 days as a function of the mass fraction of F-Lime with and without superplasticizers.



Figure 17: The compressive strength of cementation material at 28 days with and without of superplasticizer

After the figure (17) shows that the addition of superplasticizer in the matrix of cementitious material at different percentages of F-Lime significantly improves the mechanical resistance of compressive of it. This improvement is explained by the effect that the superplasticizer acts on the rheology of the mixture which is manifested by repulsion between the F-Lime and the sand grain.

#### 3.6. Gain of compressive strength at 28 days

At the end of this works, we calculated the gain of compressive strength. The figure (18) shows the gain of compressive strength at 28 days as a function of the mass fraction of limestone fillers with superplasticizer.



Figure 18: Gain of compressive strength at 28 days as a function of the mass fraction of F-Lime with superplasticizer

According to the figure (18), we observed that the gain of compressive strength increases with the increase of limestone fillers in the matrix formulation, for example, the addition of 15% and 20% of limestone fillers in our formulations increases the compressive strength by 29.5% and 28.2% respectively in comparison with the controls "M-T".

### Conclusion

In this work, we studied the influence of the incorporation of limestone fillers in the formulation of cementitious material by partially substituting the clinker of this addition at various percentages ranging from 5% to 40% by weight of cement with a step of 5%. The influence of the incorporation on the physical properties of cement paste in the fresh state was studied on one hand. The effect of the addition of limestone fillers on the mechanical properties in the hardened state was evaluated on the other hand. To improve the physical and mechanical properties asuperplasticizerof nature high water reducer and setting accelerator has been used.

The obtained results by different formulations developed to show that the introduction of limestone fillers in the formulation of the cementitious material augments finesses by a specific surface. However, the density is decreased. Similarly, we noticed that the amount of mixing water is reduced by 35% compared to the control. In addition, the ratio of W/C is decreased from 0.5 to 0.36 (chemical and granular effect). Furthermore, we have distinguished that the porosity and the capillary absorption has been decreased on one hand (granular effect). On the other hand, we have noticed that the compressive strength at a young age (2 days), median age (7 days) and long-term (28days) has been improved. This improvement represents a gain in resistance at 28 days by the 17% /26.5% /29.5% /28.2% /26.2% /23.1% /21.3% and 13.5%, corresponding of 5%-F-Lime/10%-F-Lime/15%-F-Lime/20%-F-Lime/30%-F-Lime/35%-F-Lime and 40%-F-Lime respectively. Our contribution clearly participates in the minimization of emissions of greenhouse gasses, to manufacture durable cementitious material again; ecological with mechanical and physical-chemical properties improved.

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