Journal of Materials and Environmental Sciences
ISSN : 2028-2508

JMES, 2017 Volume 8, Issue 7, Page 2302-2310

http://www.jmaterenvironsci.com /

ERVD4, 26-27 Oct 2016 Ifrane, Morocco

Development of a new cementations material eco-friendly of the environment: Study of physical and mechanical properties

M.H. R.Khudhair[a,b,*], B. Elhilal [a], M. S. El youbi[c], A. Elharfi[a]

[a] *Laboratory of Agro resources Polymers and Process engineering (LAPPE), Team of Macromolecular & Organic Chemistry, Faculty of sciences, Ibn Tofail University, BP 133, 14000, Kenitra, Morocco.*

[b] *Laboratory of Cement and Quality Control of Amran Cement Plant of Yemen.*

[c] *Laboratory of Chemistry of Solid State, Faculty of Science, Ibn Tofail University, Kenitra, Morocco*

Received 29Aug 2016,
Revised 01Oct 2016,
Accepted 04 Oct 2016

Keywords

- ✓ new materials durable cement;
- ✓ pure limestone (P, Lime);
- ✓ Composite cement (CC);
- ✓ Super-plasticizer;
- ✓ Greenhouse gas;
- ✓ Physical property;
- ✓ Mechanical strength;
- ✓ Durable development;

M.H. R.KHUDHAIR
khudhair.mohammed65@gmail.com
Phone: + 212 633 431 912

Abstract

In this work new material, durable cement based on the different percentages of pure limestone (P,Lime) and super plasticizer has been developed, partially substituting the clinker by this material in finely ground powder form. The influence of the incorporation of P,Lime on the physical chemical characteristics of cement (finesse by specific surface Blaine and density), on the physical properties of the cement paste (setting time and water content) and on the mechanical performance (compressive strength) of mortar and/or concrete to hardened State has been evaluated.

The obtained results by different methods of physical, chemical analysis showed that, the adding of P. Lime in cement increases the fineness. In more its density is decreased. We observed that, the setting time increases in function on the addition of P,Lime in the cement matrix. Similarly, the mechanical resistance to compression at a young age (2 days), median age (7 days) and long term (28 days) improve as a function of the increase in P,Lime. Most of these improvements, the addition of P,Lime in the formulation of the cement allowed us also to minimize the emission of CO_2 in the atmosphere on the one hand and win percentages of energy and raw materials consumed on the other.

1. Introduction

The productions of different types of cement are accompanied by heat and emissions of CO_2 into the atmosphere which is the main cause of the effect greenhouse. The cement industry is responsible of liberation about of 7% of CO_2 [1-3]. This amount comes from the chemical transformation process inherent in the production of clinker (a mixture of limestone and clay cooked and crushed): from 550 ° C,the formation of lime related to the decarbonation of limestone causes the release dioxide of carbon according to the following chemical reaction:$CaCO_3 \rightarrow CaO + CO_2$ [2-5]. This chemical reaction represents more than 60% of the CO_2 due to the manufacture of cements; the remaining 40% is due to transport and energy processes clinkerisation (fuel) and grinding processes.

In Yemen there are many mineral materials and natural rocks in a large quantity and a good quality. Among these, materials, we find the natural Pozzolan (PN), the pure sandstones (PS) and the pure limestone (P,Lime). This last one is located in several regions in Yemen, such as, Hadramout, Mahra, Sana'a, Amran, Etc. [6-10]. And according to statistical estimates of the ministry of oil and minerals in Yemen, these regions contain approximately reserves about of 3,6 billion m3 of P,Lime [6]. And according to the results of the chemical analyses of P,Lime, which showed that the extent of its purity, where the percentage of calcium oxide from 51,50 to 55,60%, silica from 0,03 to 4.28%, and the iron between 0,02 to 0,72% [6]. As the physical analysis has shown that the absolute density of P,Lime ranging from 2,4 to 2,7 g/cm^3, the degree of whiteness between 81,70 to 95,15% and the specific surface area between 2685 to 4488 cm^2/g, [6], which gives the material the possibility of being used in many industrial applications, such as the agriculture, the construction applications and other chemical industries.

The pure limestone is used as adding in the production of cement and various types of concrete with partially substituting the clinker by this will reduce the energy and the raw materials consumed during the production of clinker on one hand and minimize the carbon dioxide emissions into the atmosphere that the main cause of the greenhouse on the other hand.
Several works had studied the influence of the fillers of P. Lime as an aggregate on rheology properties [11-14] and mechanical performance of concrete [15-19]. In this experimental work we have achieved in the laboratory of cement and quality control of Amran cement plant (Yemen) in collaboration with the laboratory of agro resources polymers and process engineering of the faculty of science, Ibn Tofail University (Kenitra-Morocco), we substituted partially the clinker by this natural material in powder finely crushed at different percentages from 5% to 40% by weight of the clinker with a 5%. The influences of the incorporation of P,Limeon physical-chemical properties and mechanical of cementations materials have been studied. The obtained results by the different methods used show that physical chemical properties, namely fineness by the permeability of air, density, water content and setting time have been improved, as long as we have noticed a significant decrease in the mechanical resistance to compression. To improve the mechanical performance of cementations materials, we have introduced an Advanced Superplasticizer type of superplasticizer for Prolonged Slump Retention "ASPPSR402.". The results selected show significant improvement of mechanical performance with a gain of resistance to compression at 28j of 2,5% to 22%.

2. Materials and methods

2.1. Materials

2.1.1. Clinker

The type of clinker used in this work is (CMI / 42.5) from the factory of Amrancement in Yemen with 95% of clinker and 5% of gypsum. The composition chemical determined by X-Ray Fluorescence (XRF), mineralogical and the physical properties is legendary in the tables (1), (2) and (3):

Table1: Elementary chemical compositions of Clinker and gypsum

Content (%)	**Cao**	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**MgO**	**SO_3**	**K_2O**	**Na_2O**	**CL**
Clinker	62,76	21	5,84	3	1,96	0,9	1,21	0,2	0,02
Gypsum	33,4	0,7	0,36	0,09	0,63	47,2	0,03	0,1	0,01

Table2: Mineralogical composition of clinker

C_3S	C_2S	C_3A	C_4AF
47,7	25,1	10,4	9,,1

Table3: Physical properties of Clinker

Physical properties	Units	Values
Blaine specific surface	cm^2/g	3360
Density	g/cm^3	3,17

2.1.2. Sand

To prepare our mortar, we use standard sand conferring to the standard EN 196-1, delivered by the new French company of Littoral, its particle size analysis is illustrated in the figure (1).

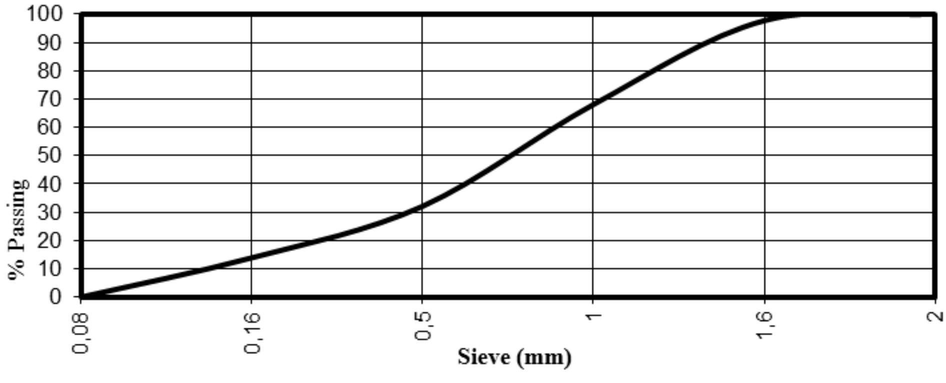

Figure 1: Grading curve of sand

The particle size analysis presented in figure (1) there is that used sand grains are distributed in a systematic way according to the standard EN 196-1 specifications [20].

2.1.3. Pure limestone (P,Lime)

The pure limestone (P,Lime) is an inorganic material that spread in many parts of Yemen, including Hadramout, Sana'a and Amran, occupying a volume about of 3.6 billion m^3. The chemical analysis determined by the X Ray Fluorescence (XRF), mineral by X-Ray Diffraction (XRD) and physical of the P,Lime of Bani Qais-Amran (Yemen) after crushing, drying for 12h at 80°C and grinding are shown in the table (4 and 5) and the figure (2).

- *The physicochemical characteristics*

The chemical compositions of pure limestone (P,Lime) after grinding determined by FRX are shown in the table. (4).

Table 4: Elementary chemical compositions of P,Lime determined by FRX

Content (%)	**Cao**	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**MgO**	**SO_3**	**K_2O**	**Na_2O**	**CL**
Pure limestone	54,96	0,621	0,12	0,159	0,411	0,0799	0,0132	0	0,0006

The mineralogical analysis by X-Ray Diffraction (XRD) of the P,Lime of Bani Qais-Amran-Yemen is shown in the figure (2).

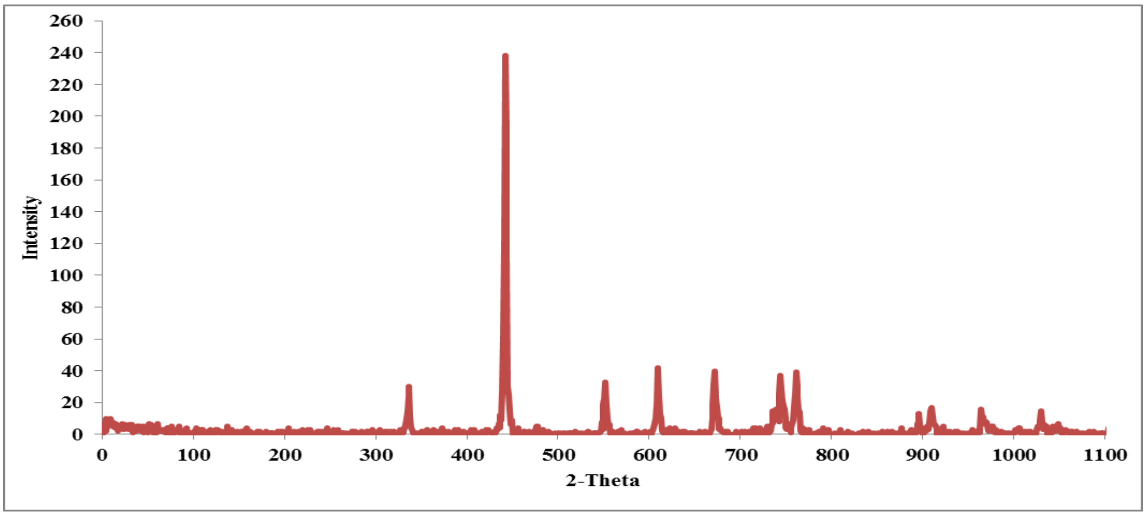

Figure 2: The spectrum by X Ray Diffraction of P,Lime

As the results displayed in the table (4) we can see that the P, Lime of Bani Qais-Amran - Yemen continues to 54,96% of lime (Cao), 0,12% of alumina, 0,159% of iron and 0,621% of silica. The results of the mineralogical analysis by X-Ray Diffraction (XRD) of the P,Lime reveal the strong presence of the lime, followed by the silica then the magnesium afterwards the oxide of the iron and the alumina.

- *The physical characteristics*

The physical characteristics of the pure limestone are given in the table (5):

Table 5: Physical properties of the P,Lime

Physical characteristics	**Units**	**Values**
Blaine specific surface area	cm^2/g	4776
Density	g/cm^3	2,13

2.1.4. Superplasticizer

In this work we used a superplasticizer of nature melamine Poly Sulfone sodium under the trade name salts ' Advanced Superplasticizer for Prolonged Slump Retention "ASPPSR402", delivered by the company CONMIX Ltd in Sharjah, United Arab Emirates, its physical properties are illustrated in table (6):

Table 6: Physical properties of ASPPSR402

Nome	Nature	Color	Density	Training area	Chloride content
ASPPSR402	Liquid	Brown	1,23	0,5-1,0	IOM

2.1.5. The mixing water

To waste our mixture, we used tap water (wells), its main features are gathered atthe table (6).

Table 7: Main features of the mixing water

Components	**PH**	**T, D, N**	**CO_3^{-2}**	**HCO_3^-**	**Calcium**	**Magnesium (Mg^{+2})**	**Conductivity**
Units	**-**	**(mg/l)**	**(mg/l)**	**(mg/l)**	**(mg/l)**	**(mg/l)**	**ms/cm**
Values	7,0	450	216,0	0,0	56,4	52,4	692,0

2.2. Methods

The formulations of different tests in maintaining the content ofgypsum to 5% of the total weight of the cement with the addition of P,Lime are presented in the tables (8 and 9).

Table 8: Composition of the fresh cement paste at base of P,Lime

Content (%)		**P-T**	**P-P,Lime 5%**	**P-P,Lime1 0%**	**P-P,Lime 15%**	**P-P,Lime 20%**	**P-P,Lime 25%**	**P-P,Lime 30%**	**P-P,Lime 35%**	**P-P,Lime 40%**
Cement	Mass (g)	500	475	450	425	400	375	350	325	300
	%	100	95	90	85	80	75	70	65	60
Pure limestone	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
	W/C	0,280	0,286	0,292	0,296	0,300	0,306	0,310	0,314	0,320

Table 9: Composition of the mortars in the hardened State used at base of P,Lime

Content (%)		**M-T**	**M-P,Lime 5%**	**M-P,Lime 10%**	**M-P,Lime 15%**	**M-P,Lime 20%**	**M-P,Lime 25%**	**M-P,Lime 30%**	**M-P,Lime 35%**	**M-P,Lime 40%**
Cement	Mass (g)	450	427,5	405	382,5	360	337,5	315	292,5	270
	%	100	95	90	85	80	75	70	65	60
Pure limestone	Mass (g)	0	25	50	75	100	125	150	175	200
	%	0	5	10	15	20	25	30	35	40
Sand	Mass (g)	1350	1350	1350	1350	1350	1350	1350	1350	1350
Water	Mass (g)	225	227	231	233	235	238	239	241	243
	W/C	0,500	0,504	0,513	0,518	0,522	0,529	0,531	0,536	0,540

3. Results and Discussion

3.1. Physical-chemical properties of cement based on different percentage of pure limestone

3.1.1. The density

The density of cement is measured by the displacement of an inert liquid towards the cement inside a graduated container. It is measured using a Le Chatelier device preferably jolting according to the norm EN 196 - 6/ASTM C188, NM 10.1.004 and calculated using the formula (1):

$$\boldsymbol{\rho} = \frac{Mass\ of cementingrams}{Absolute\ \ volume of cementin\ \ \ cm^3}\ ; \frac{\boldsymbol{g}}{\boldsymbol{cm^3}}\ \boldsymbol{(1)}$$

3.1.2. The fineness by the air permeability method (Blaine Specific Surface Method)

It is the total area of the grains contained in a powder mass [21-23], it measured using the Blaine apparatus according to the standard 10.1.005 NM. This finesse was calculated according to the formula (2):

$$S = \frac{K}{\rho} x \frac{\sqrt{e^3}}{1-e} x \frac{\sqrt{t}}{\sqrt{0,1\ \eta}}; \ \frac{cm^2}{g} \quad (2)$$

With:
P: Absolute density of cement;
K: Constant of the device;
E: Porosity (in general: 0,50);
T: Time measured in seconds;
ɳ: dynamic viscosity of the air at the test temperature

3.1.3. Ratio W / C

The aim of this test is to determine the optimum quantity of mixing water to obtain a good mortar [24-25]. This test carried out by the Vicat apparatus in accordance with the Standard 196-3.

3.1.4. Setting time

This is the time it takes for the cement paste to solidify. The objective of this test is to determine the initial and final time of cement pastebasedof the P,Lime. This experiment was carried out with the automatic Vicat apparatus according to standard 196-3.

Table 10:Physical-chemical properties of cement based on different percentage of pure limestone

Content (%)		**M-T**	**M-P,Lime 5%**	**M-P,Lime 10%**	**M-P,Lime 15%**	**M-P,Lime 20%**	**M-P,Lime 25%**	**M-,Lime 30%**	**M-,Lime 35%**	**M-,Lime 40%**
Density''g.cm^{-3}"		3,14	3,13	3,12	3,10	3,09	3,08	3,07	3,05	3,02
Fineness by specific surface area ''cm².g^{-1}"		3240	3315	3400	3570	3610	3690	3810	3920	4050
Setting time''min"	Initial	60	60	60	55	55	50	50	40	40
	Final	90	110	110	105	100	100	90	90	80
W/C	P,Lime	0,5	0,5	0,51	0,52	0,52	0,53	0,53	0,54	0,54

The results of the experimental study illustrated in the table (10) indicate that there is a decrease in the density of the cement with the addition of P,Lime relative to the control cement. As an example to 40% of P,Lime in cement, the density decreases from 3,14 g.cm^{-3} to 3,02g.cm^{-3}. This decrease is explained logically by the fact that the addition which replaces the clinker has a lower real density [22]. We also observe that the finesses of cement by the air permeability method increases as a function of the addition of P,Lime, this increase generally due to the finessesof specific surface of P,Lime.We find that the W / C ratio of our new cementation material based on P, Lime increases as a function of mass fraction of this. This increase generally due to the chemical and mineralogical composition of our addition which is rich in CaO; On the one hand the presence of high levels of CaO influences the phenomenon of hydration because a limestone rich in this mineral phase tends to have a higher water demand and on the other hand linked to the fineness of the addition. We also noticed that the presence of fillers of the limestone in the cement acts favorably on the physical properties of our new cementation material based on P, Lime, namely the initial and final time of setting. This last has been considerably reduced as a function of the percentage of P,Lime and which gave our binder the role of accelerator of setting. This decrease in the setting time due generally to the chemical and mineralogical compositions of our addition which is rich in Cao and low in Al_2O_3 on the one hand and on the other hand it is due to the fineness of limestone fillers that fills the voids between the cement particles, which improves the compactness of the concrete subsequently.

3.2. Influence of P,Lime on the mechanical properties of mortar and / or concrete

We also evaluated the influence of P,Lime on the mechanical performance of mortar and / or concrete using the mechanical resistance to compression 'Compressive strength'. The measurements of 'Compressive strength' are carried out on standardized prismatic specimens (4x4x16) cm^3 according to the specification of the standard (NF EN 196-1) [20], the specimens are removed from the mold after one day and stored under water, At the age of crushing. The measurement of ‘compressive strength' was carried out at an early age of '2 days', in the medium term, '7 days' and in the long term '28 days' in order to observe the progressive mechanical performance of our new cementation material. Base of P,Lime as a function of time, the 'Compressive strength' is calculated using the following formula: $\text{Compressive strength} = (\text{Load in N}/\text{Area in mm2}); \text{MPa}$.

The figure (3) presented the variation of the compression strength as a function of time in days.

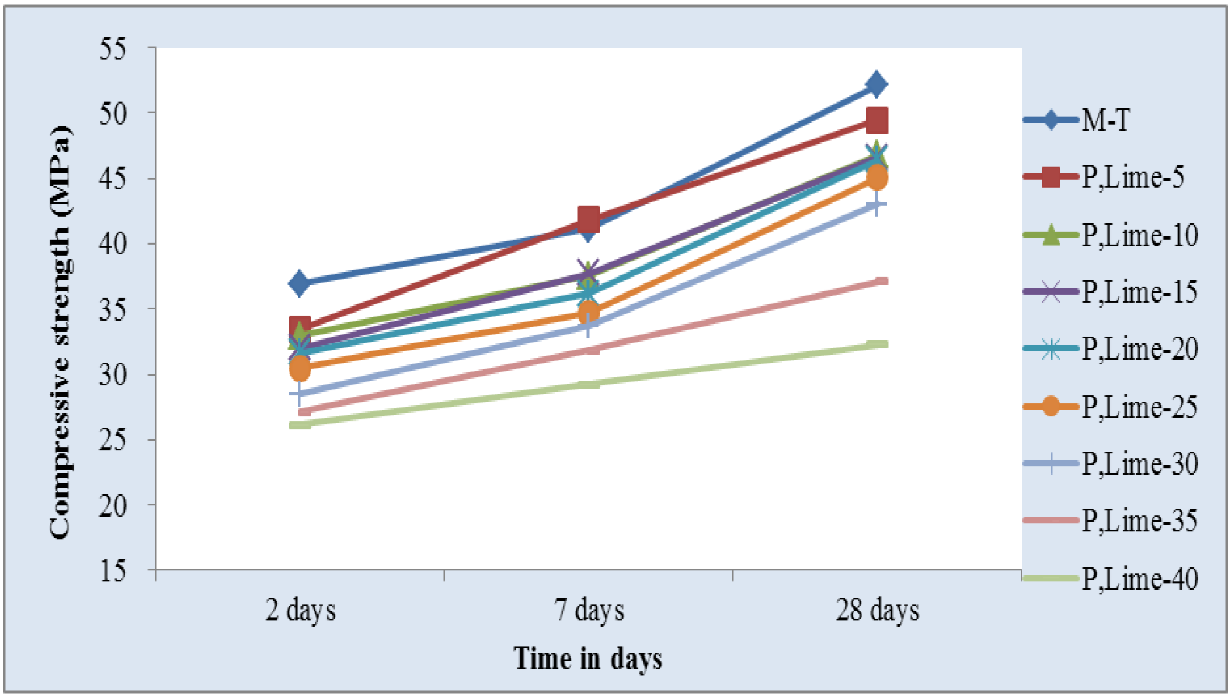

Figure 3: Variation of the compression strength of our cementation material based on P,Lime as a function of time in days

From the figure (3) we can deduce the following remarks:

- The 'Compressive strength' of all mortars based on P,Lime increases steadily with age and shows no falls.
- The 'Compressive strength' decreases considerably with the percentage increase in the addition of P.Lime to 2/7 and 28 days. For example, a substitution of clinker by 40% of P,Lime, the 'Compressive strength' decreases by 29,25%, 29,08% and 38,11% for 2d / 7d and 28d respectively as shown in figure (3).

To improve the physical and mechanical properties of our cementationmaterial based of P,Lime such as compressive strength and the report W/ C, we have carried out a series of formulations with varying percentages of 0,5% to 5% by weight superplasticizers of the cement with a pitch of 0.5%. The results obtained showed that 'compressive strength' increases with the addition of 0,5 to 3,5% of ASPPSR402 beyond these percentages, the 'compressive strength' decreases considerably. This shows that the 3,5% is the saturation point. Then, we selected the 3,5% of ASPPSR402 and we introduced it in our formulations with different mass fractions of P,Lime of 5 to 40%, the figure 4 illustrates the evolution of the 'compressive strength' of our new cementation material based on P,Lime with 3,5% of the ASPPSR402 as a function of time.

The figure (4) shows the variation compression strength of our cementation material based on P,Lime with 3.5% ASPPSR402 as a function of time in days

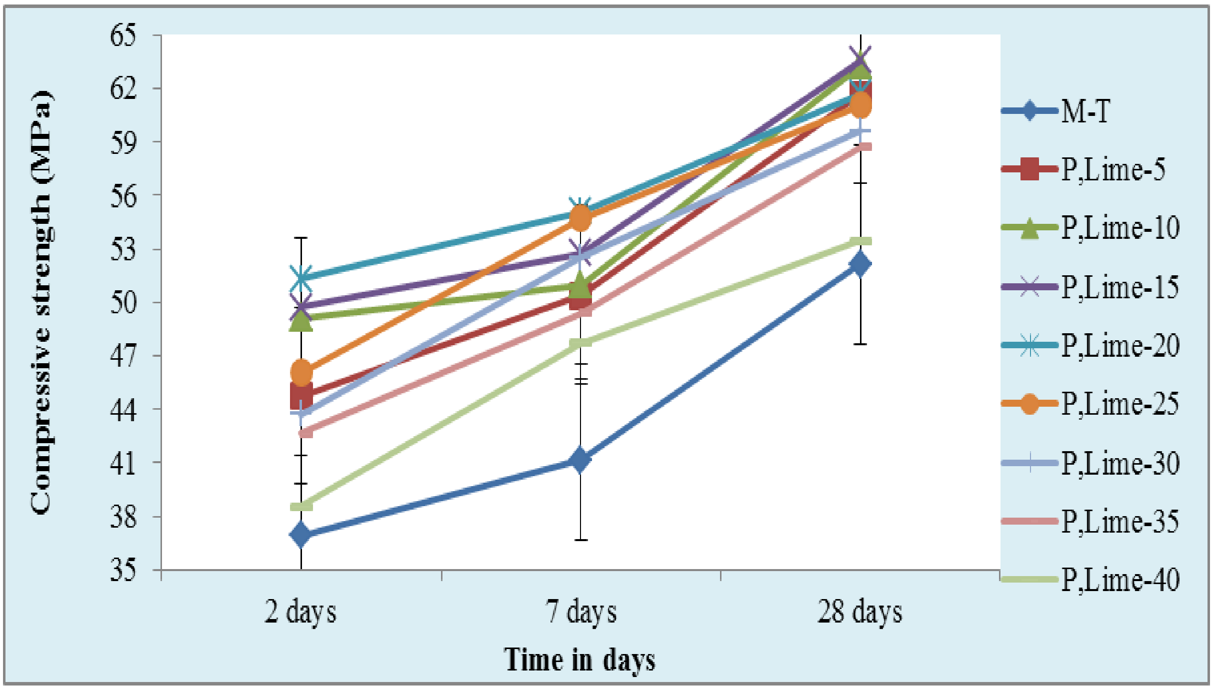

Figure 4: Variation of the compression strength of our cementationmaterial based on P. Lime with 3.5% ASPPSR402 as a function of time in days

From the figure (4), which illustrates the variation of compressive strength as a function of time, we observed that at young, medium and long-term the compressive strength increases with the addition of P,Lime with 3.5% of the ASPPSR40. This increase is explained by the fact that the addition of superplasticizer to the cement matrix manifests itself by dispersing the grains of the binders, whichfacilitates, on the one hand, the hydration of the mixture during kneading operations and improves the compactness of this material Share.

And finally we calculated the compressive strength' at 28 d of our new cementation material based on P, Lime at various percentages ranging from 5 to 40% with and without ASPPSR40.

The figure (5) illustrates the evolution of compression strength at 28 days without of superpalsticizer and with superpalsticizerof our new cement material based on different percentages of P,Lime ranging from 5 to 40% P,Lime.

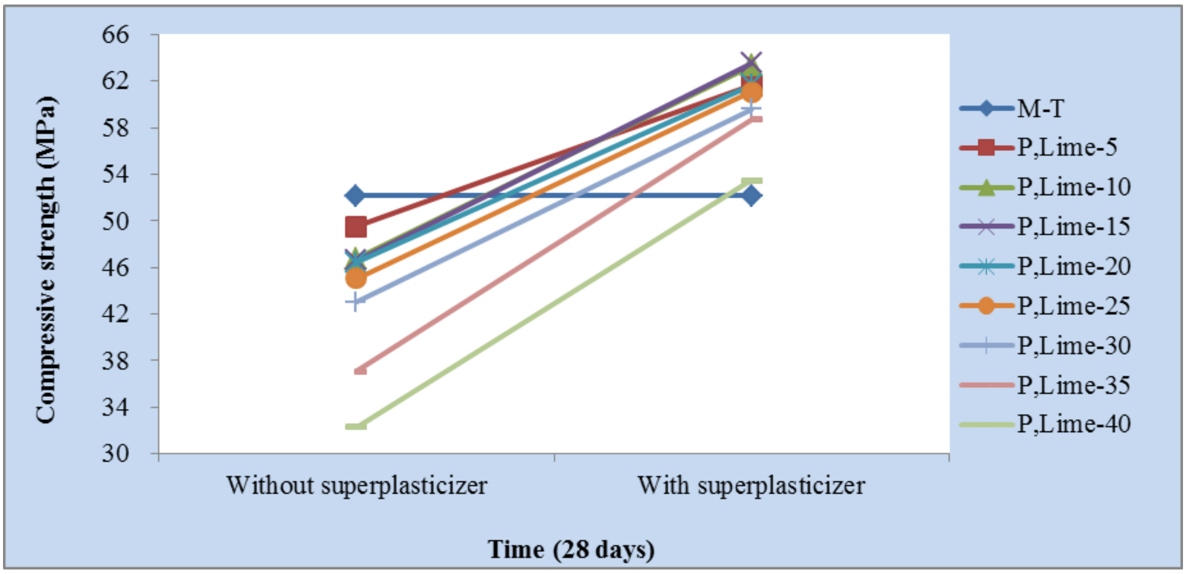

Figure 5: Evolution of compression strength of our new material cementations based on P,Lime as a function of the age in days

According to the Figure 5, which shows the variation of the compressive strength at 28 days of the formulations with and without superplasticizer, we observe that the addition of ASPPSR40 in the cementations matrix based on P,Lime- significantly improves to the mechanical performance of this one. This improvement is explained by the effect of ASPPSR40 on the theology of the mixture, which is manifested by a repulsion between the grains of cement and P,Lime, generating good fluidity with a minimal amount of water, high compactness and subsequently improved compressive strength.

3.3 Gain of the compressive strength at 28 days

We calculated the gain of 'Compressive strength' at 28 days using the following formula:

$$\frac{R_{mcx}-R_{mct}}{R_{mct}}\boldsymbol{x100} \quad (4)$$

Or:

R_{mct}: Controlcompressive strength at 28 days mortar;

R_{mcx}: Compressive strength of mortars with P. Lime and ASPPSR40, and X = 5%, 0% 40%;

The figure (6) shows the gain ofcompressive strength at 28 days.

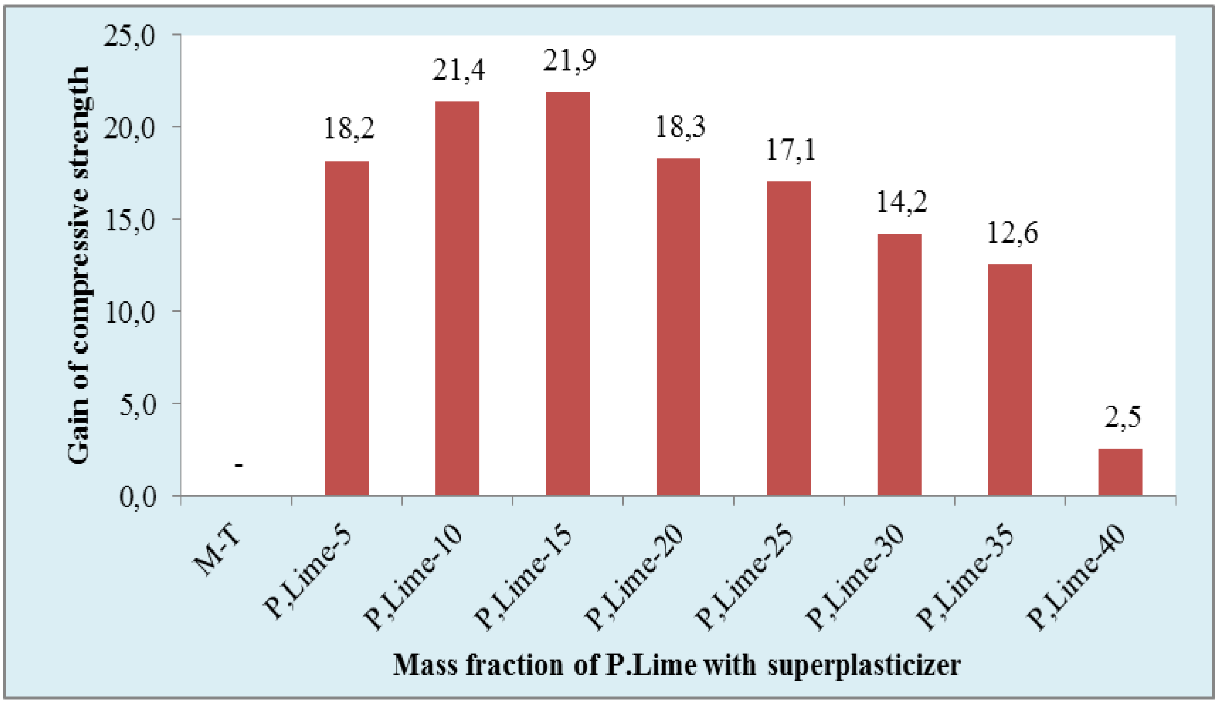

Figure 6: Gain of compression strength at 28 days as a function of the mass fraction of P,Lime with 3.5% of ASPPSR40

According to the graph (6) which shows the gain of compressive strength as a function of the% addition of P,Lime with 3.5% ASPPSR40, we have observed that the formulations containing 3.5% ASPPSR40 show a high compressive strength compared to the control. With a mechanical strength gain at 28 days; 18.18%, 21.38%, 21.88 %, 18.30 %, 17.09 %, 14.24 %, 12.58% and 2.52 % of samples of 5% P,Lime / 10% P,Lime / 15% P,Lime / 20% P,Lime / 25% P,Lime / 30% Cal / 35% P,Lime and 40% P,Lime respectively.

Conclusion

During this work, we have studied the influence of the partial substitution of clinker by pure limestone (P,Lime) on the physical chemical characteristics of cement, physical properties and compressive strength ofcementations material base of P,Lime. The study highlights on the dependence between the replacement of part of the clinker by the pure limestone at different percentages and the properties of the cement. It is particularly the fineness by specific surface area, density, water demand, setting time and compressive strength. Indeed the analyses, physical, chemical and mechanical of cement at base of P. Lime showed that up to 40% of pure limestone, cement properties are adequate by international standards. The obtained results by the different methods of physical,chemical analysis showed that the P,Lime adds in cement increases fineness by specific surface. More density is decreased. We noticed that setting time believes when the percentage of the P,Limeincreases. Similarly, the compressive strengths at 2 days/ 7 days and 28 days are improved as a function of the increase in pure limestone in the presence of 3.5% ASPPSR40. The new materials based on P,Lime contribute favorably to the minimization the emissions of CO2 into the atmosphere and to the reduction of energy consumption and raw materials. Subsequently to produce eco-friendly of the environmental cementations materials.

References

1. Khudhair m. H.r., elyoubi m. S.,, Elharfi A., *J. Mater. Environ. Sci.*, 8.3 (2017) 902-910.
2. Shahrabadi H., Nikoo H. S., Forsat M., *J. Mater. Environ. Sci.*, 8.2 (2017) 457-466.
3. khudhair m., el harfia., *Inter. J. Ch.Tech. Res.*, 9.12 (2016) 695-704.
4. Fan Y.,Zhang S., Wang Q., Shah S.P., *Constr. Bui. Mater.*, 102 (2016) 486-495. .
5. Guendouz M., Debieb F., Boukendakdji O., Kadri EH., Bentchikou M., Soualhi H., J. Mater. Environ. Sci., 7 (2016) 382-389.
6. Gouasmi M.T., Benosman A.S., Taïbi H., Belbachir M., Senhadji Y., *J. Mater. Environ. Sci.*, 7 (2016) 409-415.
7. Hamadache M., Mouli M., Bouhamou N., Benosman A.S., Chaib O., Dif F., *J. Mater. Environ. Sci.*, 7 (2016) 416-421.
8. Chaib O., Mouli M., Hanifi M., Hamadache M., *J. Mater. Environ. Sci.*, 7 (2016) 422-428.
9. Ziegler M. H., *Gu. Petro. Bahr.*, 6 (2001) 445-505.
10. Taib M., *Adv. Rel.*, (2012) 60-67.
11. 6. Taib M., *Advance Release.*, (2013) 621- 627.
12. Aly M., Hashmi M S J., Olabi A G., Messeiry M., Hussain A I., *Mater. Sci. Eng: A.*, 528 (2011) 7991– 7998.
13. TopÇU I B., Uğurlu., *Cem. Concr. Res.*,33 (2003) 1071 – 1075.
14. Lothenbach B., Saout G., Gallucci e., ScrivenerK., *Cem. Concr. Res.*, 38 (2008) 848-860.
15. Svermova L., Sonebi M., Bartos P J M., *Cem. Concr. Compos.*, 25 (2003) 737-749.
16. Ashori A., TabarsaT., Valizadeh I., *Mater. Sci. Eng: A.*, 528 (2011) 7801– 7804.
17. Voglisn.,Kakali g., Chaniotakis e., Tsivilis S., *Cem. Concr. Compos.*, 27 (2005) 191-196.
18. Yahia A., Tanimura M., Shimoyama Y., *Cem. Concr. Res.*, 35 (2005) 532-539.
19. Çelik T., CA K., *Cem. Concr. Res.*, 26 (1996) 1121-1130.
20. Benbarek S., Bouiadjra B., Achour T., Belhouari M., Serier B., *Mater. Sci. Eng: A.*, 457 (2007) 385–391.
21. European Committee For Standardization., European standard., EN 196-1, (1995) 15-471 P.
22. European Committee For Standardization., European STANDARD., EN 196-2 (1995) 15 -472.
23. Agustin H H., *Science & Technology.* 30 (2009) 61-66.
24. Arjunan P., Kumar A., *Cem. Concr. Res.*, 24 (1994) 343 – 352.
25. Voglisa N., Kakalia G., Chaniotakisb E., Tsivilisa S., *Cem. Concr. Compos.*, 27 (2005)191-196.

(2017) ; http://www.jmaterenvironsci.com