Journal of Materials and Environmental Sciences
ISSN : 2028-2508

JMES, 2017 Volume 8, Issue 7, Page 2541-2548

http://www.jmaterenvironsci.com/

Effect of clinker free lime and cement fineness on the cement physicochemical properties

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Received 02 Nov 2016,
Revised 29 Mar 2017,
Accepted 02Apr 2017

Keywords

- ✓ Free lime,
- ✓ Cement fineness
- ✓ Cement,
- ✓ Compressive strength,
- ✓ Normal consistency,
- ✓ Setting time,
- ✓ Expansion

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Abstract

This research aims to clarify the effect of free lime content and the cement fineness on the cement physicochemical properties. The free lime content by a titration method was observed and the cement fineness was determined by sieving at 40µm. A detailed experimental program was carried out in order to evaluate the extent to which free lime content in clinker and cement fineness can be tolerated. Some basic and durability properties of cement with varied free lime contents and fineness were considered. The studied basic properties consisted of normal consistency, autoclave expansion, initial and final setting time also compressive strength. Two distinct types of cements were obtained from two different sources, and free lime was added to obtain overall free lime contents in order of < 2% and > 2%. The cement fineness at 40µm was varied between 17.0 and 31.9%. Experimental results revealed that physical properties such as normal consistency and water requirement were affected by free lime and by cement fineness that had slight chemical effects on cement properties, i.e., faster setting, lower compressive strength, especially at early age, and higher autoclave expansion. Regarding durability, mixtures with the high free lime clinker led to higher expansion due to alkali-aggregate reaction. The expansion was smaller than that of cement prepared with clinker which has free lime content lower to 2%.

1. Introduction

The Portland clinker is the base material of the cement manufacture [1]. It consists at least of two thirds (by weight) calcium silicate [$SiO_2(CaO)_3$]: C_3S, [$SiO_2(CaO)_2$]: C_2S and the remaining part contains the oxide iron (Fe_2O_3), the aluminum oxide (Al_2O_3) and other oxides. Clinker quality requires a mass ratio (CaO)/(SiO_2) which is less than 2, a C_3S contents are above 50% and a lime saturation factor is between 90 and 98% [2]. Determining the content of free lime is especially important to judge doneness and clinker quality [3-5]. The free lime limit isn't the same for all cements; it depends on several factors, especially the temperature reached during the cooking and the grains distribution in cement after grinding. Clinkers cooked are result from a raw meal which is well balanced and have good granulometry that is below 2% [6].

The increases of clinker free lime content may originate from a disorder of the cooking process (insufficient curing temperature, decomposition of Alite caused by overcooking or a too slow cooling of the clinker, reducing conditions in the cooking zone, ...) or the failure in preparing the raw (high level of lime saturation factor (LSF), coarse grinding or heterogeneity of flour ...) [7-10]. When the lime saturation factor is greater than 100%, there is an imbalance between the constituents. All the lime can be saturated and remain in the uncombined form of lime or free lime which causes delayed expansion's mortar and concrete. It causes also a serious deterioration of structures built. Several studies have focused on limiting the free lime content in fly ash [11] and their effect on the concrete mineralogy [12]. Other studies have shown that the alkali present in the various cement components have adverse effects on its quality [13-16].

Studies conducted on the effect of clinker free lime on the cement properties were very low and for the purpose of producing quality material, we studied the effect of the clinker free lime on the cement physicochemical properties, like: the expansion, the setting time and the compressive strength. For this, two types of clinker were used to produce cements study. The first type has a clinker free lime content is less of 2% and the second type has a high content of free lime (unburnt). The corresponding cements of the two clinker types were prepared with an identical proportion of additions to eliminate their effects on the cement physicochemical properties. The results have shown that the clinker free lime has a great effect on the expansion and the compressive strength of the cement.

2. Experimental details

2.1.*Materials*

- Limestone and gypsum (additions) are taken from a cement mill doser (BK_{IV}) and they dried in an oven at 105°C and 60°C, respectively to facilitate crushing and to prevent clogging in the mill.

-Fly ash is taken from a cement mill doser (BK_{IV}). They have a dry fine nature and they don't need any grinding or drying.

The two cements types that we had studied are:

- The first type is taken from the production chain of the HolcimRas El Ma company: Eight samples of clinker and cement corresponding were taken from cement doser mill BK_{III} which we designate by C_{IIIi}, with i varies from 1 to 8 (Group G_1) and the other three samples were removed under cement doser mill BK_{IV} which we denote by C_{IVJ} with j varies from 1 to 3 (Group G_2).

- The second type is prepared in the HolcimRas El Ma laboratory from the clinker unfired. This clinker was taken from the hopper of unburnt which has high free lime content and it was milled in HOLCIM grinding with gypsum limestone and fly ash in identical levels of those samples of the first cement type. The eight samples were designated by: C_k with k varies from 1 to 5. Samples C_3, C_4 and C_5 are assigned SB suffix to denote that they have suffered over grinding to achieve the desired fineness (G_3 Group).

The difference between these two types of cement is the fact that we have prepared cements that have a free lime content that exceeds 10%.

2.2 *Preparation of cement*

To avoid the effect of the percentages variation of the mixture constituents, we maintained those proportions constant for all samples, taking into account the humidity of limestone and gypsum which are 7.2% and 5.56%, respectively. The mixture is composed of: 26.64% limestone, 7.75% gypsum, 5.13% fly ash and 60.48% of the clinker. We prepared mixtures of 3kg for each sample. This amount has prepared 3 sets of trying.

Thereafter, each sample was separately ground in two types of mills. The first milling is done with a ball mill which is constituted a cylindrical chamber with horizontal axis and a capacity of 20kg. It was used to prepare cement samples with a fineness primary. The second milling was performed by using the HERZOG mill in order to have a constant Blaine fineness comparable to the product manufactured industrially.

The milling was stopped after every two operation (3 minutes for each one) in order to cool the grinding plate, to keep temperature below 80°C and to avoid dehydration of gypsum during this operation.

2.3 *Chemical analysis by X-ray spectrometer*

Quantitative elemental analysis of the clinkers and cements manufactured is carried out by X-ray fluorescence and through 8460S spectrometer (Table 1). Sample preparation involves surbroyer. 20g of the material was treated with two drops of tri-ethanol amine for 3mins in HERZOG mill.

2.4*Determination of the free lime content*

It aims to control the uncombined lime in clinker or in cement (Table 1) by its extraction with ethylene glycol and its dosage acidimetrically following, the assay reactions:

$$(CH_2OH)_2 + CaO \rightarrow (CH_2O)_2^{2-} + Ca^{2+} + H_2O \qquad (1)$$

$$Ca^{2+} + 2HCl \rightarrow CaCl_2 + 2H^+ \quad (2)$$

2.5 Size Study (Refusal)

This study consists to determine the percentage of grains according to size and by using the laser granulometer.

The percentage of refusal is given by:

$$\%R = m \times \frac{100}{10} \qquad (3)$$

m : Refusal mass of 10 g of the material

Table 1: Chemical and mineralogical composition of clinker and cement

Elements Sample	Clinker								Cement			
	C_3S	C_2S	C_3A	C_4AF	MgO	K_2O	SO_3	CaO_L	MgO	R_{40} %	R_{90} %	SO_3
C_{III1}	58.8	18.4	9.3	10.4	1.32	0.91	0.97	1.73	1.26	19.5	4.2	2.96
C_{III2}	62.1	15.4	8.8	10.7	1.47	0.82	0,68	1.33	1.37			2.89
C_{III3}	60.9	16.7	8.8	10.6	1.31	0.88	0.81	1.39	1.36	19.1	4.0	2.97
C_{III4}	60.2	17.7	8.7	10.6	1.29	0.88	0.75	1.61	1.33	19.9	4.4	3.02
C_{III5}	60.2	17.6	8.7	10.6	1.30	0.84	0.74	1.42	1.37	20.2	4.2	3.0
C_{III6}	61.1	16.1	8.4	11.4	1.42	0.84	0.97	1.86	1.35	19.8	4.5	3.34
C_{III7}	60.0	16.8	9.3	10.7	1.40	0.77	1.08	2.18	1.34	22.1	5.4	3.57
C_{III8}	60.6	16.2	9.2	10.7	1.41	0.78	1.08	2.11	1.32	21.4	5.8	3.56
C_{IV1}	63.0	13.8	8.7	11.0	1.60	0.88	0.79	3.46	1.72	20.7	5.6	3.22
C_{IV2}	62.2	14.7	9.2	10.2	1.63	0.81	0.85	3.68	1.61	17.0	1.2	3.51
C_{IV3}	62.0	14.9	9.3	10.2	1.67	0.88	0.84	3.82	1.61	17.5	1.2	3.51
C_1	62.2	8.3	8.5	14.15	2.06	0.88	5.21	5.33	1.94	17.8	1.2	7.06
C_2	62.2	8.6	8.8	13.7	2.41	1.44	4.82	9.04	2.2	19.9	6.3	6.64
C_3	70.3	1.7	9.1	11.4	2.30	1.39	4.25	11.27	2.11	20.9	6.4	6.10
C_{3SB}										31.5	8.9	
C_4	71.3	2.1	9.1	10.4	1.33	1.33	3.61	14.66	2.07	19.2	3.4	5.63
C_{4SB}										29.2	8.7	
C_5	68.6	5.1	9.6	10.0	1.34	1.34	3.49	16.15	1.94	19.3	5.4	5.27
C_{5SB}										31.9	8.4	

2.6 Setting time test

The setting time test is to follow the evolution of the consistency of a standard paste. The VICAT apparatus is used in this case and it's equipped with a needle of 1.13mm in diameter. Under the effect of a load of 300g, the needle stops at a bottom of the distance d = 4mm ± 1mm from the mold which mean that the initial setting is achieved. The time measured from the start of mixing in until when the needle was stopped, is called "START SETTING TIME". The "END SETTING TIME" is the time when the needle doesn't penetrates more than 0.5mm. The test must be conducted in a room whose temperature is 20 ± 1°C and the relative humidity is above 90%. The procedure of this test is determined according to the NM 10.1.005 standard [17].

2.7 Expansion test

This test is realized to assess the increase in volume caused by calcium oxide or magnesium, contained in the cement, during the hydration reaction. Such test ensures that cement doesn't contain substances which could create a dangerous expansion over time. According to NM 10.1.005 Standard, the apparatus used to measure the expansion is the mold of Le Chatelier. This test consists to make a paste of standard consistency and which will be introduced in two molds of expansion. After filling, the molds are kept 24 hours in the wet cabinet. After this time, we should measure the spacing between the tips of the needles. Then the molds are immersed in water which is gradually brought to boiling. After boiling for three hours, we measured again the final separation of the needle points without waiting the cooling of samples. The expansion is characterized by the increase in the spacing of the ends of the two needles.

2.8 Compressive strength

The test is constructed in accordance to the NM 10.1.005 standard and it consists to study the compressive strength of mortar specimens. This mortar is formed from 1350g of standard sand, 450g of cement and 225g of mixing water (W/C = 0.50). The essays are performed on the prismatic specimens of 4 x 4 x 16cm which were packed in humidity cabinet at 20°C. After 24h of time mixing, these test pieces are demoulded after being stored in water at 20±1°C until the burst test at 2, 7 and 28 days. The mechanical compressive strength is determined on a PERRIER apparatus type with a force of 240daN/s.

3. Resulats and Discussion

3.1. Effect of the free lime content on the cement expansion

The following figure (Figure 1) shows the evolution of the normal cement paste expansion (W/C varies from 0.26 to 0.5) in function of the clinker free lime content. To avoid the effect of particle size, all the samples have the same particle size (R_{40}~20% and R_{90} ~5%).

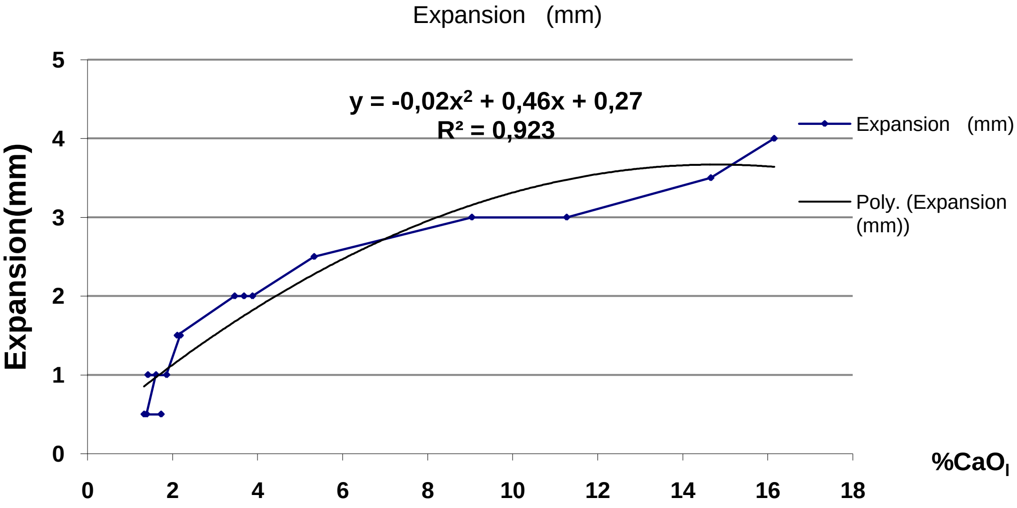


Figure 1: Evolution of the expansion cement in function of the clinker free lime content

The figure above shows an increase in the cement expansion with the clinker free lime content. The shape of this curve seems to represent the square root function of the free lime content. This function is the evidence of the cement expansion increase which is proportional to the square root of the clinker free lime content. And this function takes the following form:

$$Y = -0.02x^2 + 0.46x + 0.27 \quad (4)$$

The correlation coefficient R^2 of this equation is of the order of 93% which shows that this model is significant and representative of this study.
Indeed, the hydration of free lime by Topochemical way (without dissolution), is accompanied by a change in the crystallization system and by a significant increase in the apparent volume of free lime. This leads to the development of the enormous pressures within the cement matrix and thus causes the increase of its expansion which results in the progressive deterioration of concretes made with this cement type. The high concentrations of free lime cause the production of small Ettringite crystals and the expansion development. This increased expansion of the finely ground samples is probably due to the fact that the part of the free lime isn't participating in expansion process, because it dissolves in the mixing water and it precipitates as Portlandite or it leads to the formation of the CSH by the Pozzolanic reaction with the fly ash silica (used as additions).

3.2. Effect of free lime content and finesse on the cement expansion

For E/C ~ 0.4 à 0.5, a remarkable increase (Figure 2) of the cement pastes expansion was showed after coarse grinding (R_{40} ~ 30% and R_{90} ~ 9%) and before achieving the desired fineness which is R_{90} ~ 20% and R_{40} ~5%.

The increase in expansion of the cement pastes (R_{90} ~30% and R_{40} ~9%) compared to the overground cement pastes (R_{90} ~ 20% and R_{40} ~ 5%) results from a late hydration of free lime remaining inside the clinker grains that weakly crushed. This increase is more important when the clinker grains are small. This could also result from the formation of secondary Ettringite at the later moment of cement hydration when the cement paste reaches a certain rigidity by Topochemical reaction of the calcium aluminates which are in the grains of the weakly crushed clinker and those whose dissolution is slowed down by the formation of primary Ettringite in the early stages of cement hydration. Indeed, creating the space necessary to contain the secondary Ettringite (denoted Ettringite type II) is carried out by a bulk increase of the specimens. According to Mehta [18], the Ettringite type II is composed of small rod-shaped crystals of 1 to 2µm in lengthiness and 0.1 to 0.2µm in thickness. They are formed under conditions of high concentration of hydroxyl ions during the Portland cement hydration and they have great influence on the expansion and on the resistance of cement.

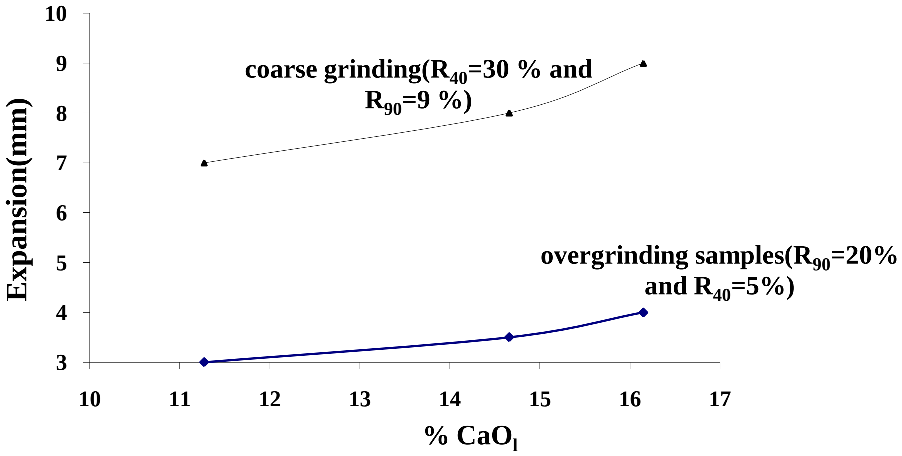


Figure 2: Effect of clinker free lime content and cement fineness on the cement expansion

3.3. Effect of free lime content on cement compressive strength

Figure 3 presents the compression tests results of prepared mortars with different cements types. Its shows that for all maturities time (2, 7 and 28 days), the cement compressive strength increases slightly to reach the maximum values (~ 35MPa) at levels of the free lime content which is close to 3.5% (samples of the group G_2), then it decreases with the increasing of the free lime content (for the contents which are higher than 4%, samples of group G_3). For free lime content equals to 2% (samples of group G_1 and G_2), the values of the mortars compressive strength are gathered in a narrow region which shows a constant quality of the industrial product.

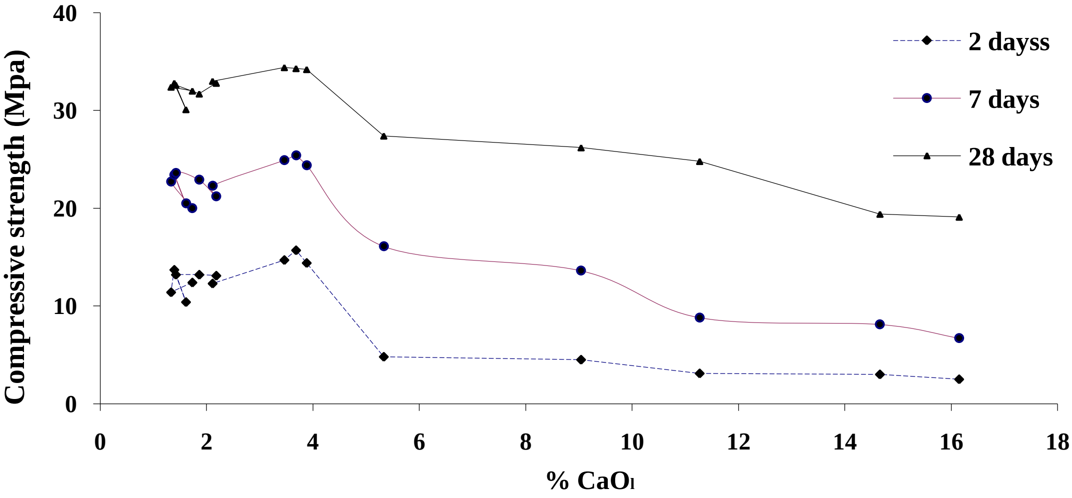


Figure 3: Evolution of the cement compressive strength in function of the clinker free lime content

The slight increase of mortars compressive strengths of group G_2, compared to the group G_1 can be derived, firstly to the high degree of grinding fineness taken out of the vertical cement mill (BK_{IV} which gives a high fineness), and secondly to the participation of the Portlandite in the improving of the cement mechanical strength by filling the pores of the cement matrix.

For high free lime contents, there is precipitation of a high rate of Portlandite in the cementitious matrix. This increased rate of Portlandite has resulted by reduction of the cured mortar mechanical strength. In addition, the disturbances caused by the various reactions and the products formed as a result of a high content of SO_3 (group G_3), lead to a loss of mechanical strength.

Indeed, the presence of free lime favors the colloidal Ettringite precipitation. This Ettringite has particular properties, such as a large absorption number of water molecules that are placed between the hydrophilic columns of AFt which causes swelling of its structure by electrostatic repulsion and fall cohesive forces. The balance (interstitial solution + mineral) can be controlled in a first approximation by the Portlandite. The presence of a high concentration of Ca^{2+} and SO_4^{2-} ions in the pore solution favors the formation of Ettringite and gypsum.

The gypsum solubility ($CaSO_4 . 2 H_2O$) isn't very high (5.10^{-3}mol / l at 25°C), so that the mineral precipitates easily in abandoned areas of the cementitious matrix (pore, cracks). It is frequent to find "Gypsum veins": abundant precipitation of gypsum is localized at the cracks in the cement matrix. The crack isn't assigned to the gypsum but its presence is caused by the precipitation of AFt (PLANEL D) [19]. The Gypsum would influence the overall loss of the cement matrix cohesion (decalcification of C-S-H) and it may block the formation of a porosity portion. The Ettringite would be responsible of the tensile stresses which can create cracks in the cement matrix (facilitated by the loss of strength which is caused by the precipitation of gypsum).

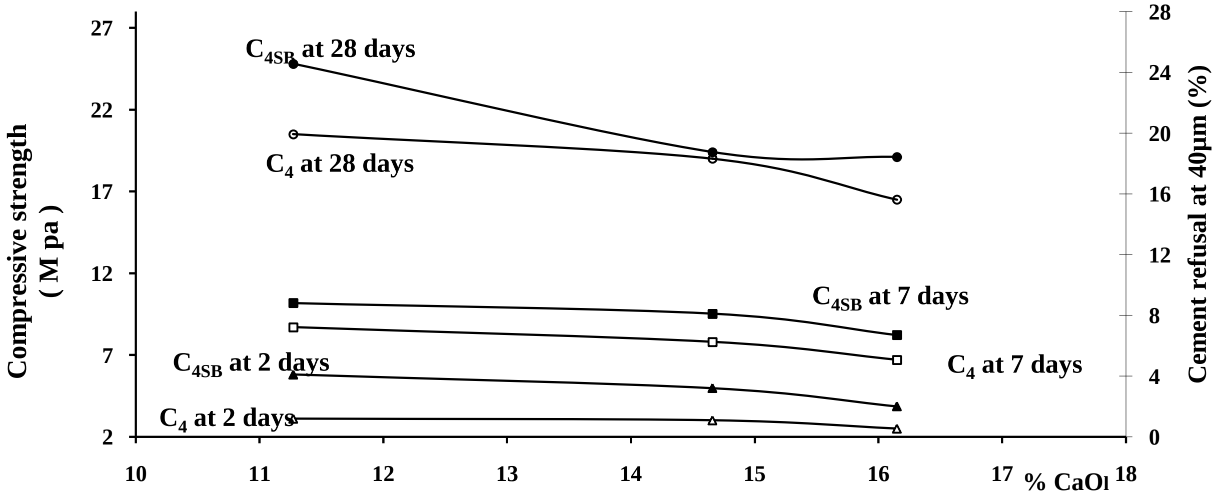
The cementitious matrix cohesion and the development of mechanical properties, are the results of the entanglement of crystals, the existence of solids ports (crystalline) or liquid ports (water content) and the surface forces (hydrogen bonds or Van der Waals) [20]. The cohesion forces are the responsible of the development of the cement paste mechanical strength and they can be classified in order of decreasing intensity:

C-S-H>CH>AFm and AFt.

Furthermore, the most important parameter that controls the formation of the CSH, is the amount of CaO dissolved (which sets the pH of the solution) when silicates hydration is produced. Ca/Si ratio of CSH continuously increases when the concentration of the free lime pass from 6 to 20mmol/l and it remains constant at 22mmol/l (pH= 12.5) which corresponds to the precipitation of Portlandite ($Ca(OH)_2$). Then, Ca/Si ratio continuously increases again in a supersaturated environment of lime ([CaO] = from 22 to 35mmol/l) [21-22].

3.4. Effect of particle size on the cement mechanical strength

For samples which have the same clinker free lime content and cement grinding fineness, play a role in the cohesion of the cement matrix by increasing the reactive surface, in particularly for the age of 28 days (Figure 4).



**SB suffix to denote that they have suffered overgrinding to achieve the desired fineness (G_3 Group)*

Figure 4: Effect of cement fineness on cement strength for 2, 7 and 28 days

Particle size is one of the most important parameters that affect the hydration and setting process of cements. The change in cement particle size affects some key characteristics of the cements such as its setting time, compressive strength, morphology, and phase composition.

As the results of this investigation indicate, cement compressive strength is associated with the solid network formation, influenced by the rate of the hydration process. The required energy for forming this solid network is provided by the surface energy produced from formation of product material in the liquid phase. Thus, the higher rate of hydration reaction leads to higher supersaturation rate and consequently, amelioration in cement compressive strength. Although the quantity of hydration product was a main factor affecting the macro-properties of the cement, the compressive strength was associated with the porous structure and the matches of all particles. Dehydrated particles took part in matches among the grains as the ‘‘micro-framework’’. The smaller the grain of the starting material, the faster the hydration process, and the more hydration product would be formed. In the presence of proper quantities of framework material, the adhesive strength among the grains would rise, and so would the value of the compressive strength at macroscopy. Otherwise, a fast hydration reaction would produce more defects in the hydration product crystal, which would make it difficult to reach thermodynamic stability. Such metastable particles would reach thermodynamic equilibrium through a dissolution-reprecipitation process, which might destroy the existing structure of setting cement slurry formed at the initial stage and decreases the compressive strength [23-26].

3.5. Consistency of mixing and free lime

For the clinkers with free lime contents less than 4%, the amount of water required to form a normal paste which is almost constant and close to 26%. For those having CaO_l contents exceeding to 5%, the mixing water demand increases proportionally to the free lime content which reaches 52% for 16% of free lime content. Clinker samples of the group G_3 bring a considerable amount of sulfur which has a very high affinity for potassium. The formed potassium sulfate tends to combine with the first sodium sulfate in order to form the Aphthitalite ($K_3Na(SO_4)_2$). The surplus of Potassium sulfate is associated with calcium sulfate to form Langbeinite ($CaK_2(SO_4)_2$) and the residue potassium Sulphate remains as Arcanite K_2SO_4.

The samples of group G_3 contain a high content of K_2SO_4 which can cause precipitation of Syngenite and the increase of the mixing consistency (Eq. 5).

$$K_2SO_4 + CaSO_4, 2H_2O \rightarrow CaK_2SO_4, H_2O + H_2O \quad (5)$$

An additional amount of water is necessary for free lime hydration present in the samples and that makes the increase in mixing consistency which is more important when the free lime content is high (Figure 5). The cement fineness contributes also to the increase and the improving of the material reactivity.

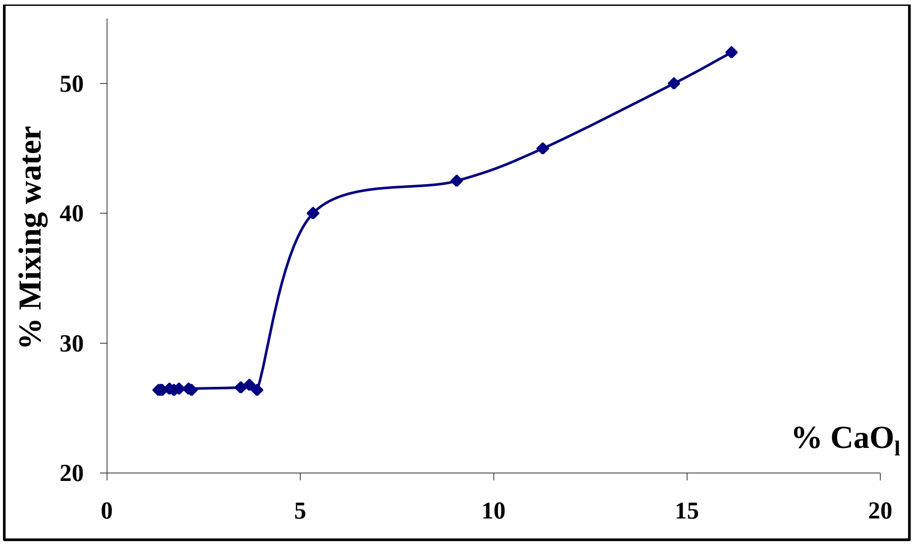


Figure 5: Effect of free lime content on the cement mixing consistency

3.6. Quick-setting cement

The initial and the final setting time of the groups G_1 and G_2 are normals, while the samples of the group G_3 present a fast setting. This may be due to the surplus of sulfate ($CaSO_4$) which is present as soluble anhydrite and it dissolved in the clinker phases. A parameter used as first discrimination of sulfur in the clinker is represented by sulfates module (m.s).

$$m.s = \frac{SO_3}{1.29} Na_2O_{eq} \qquad (6)$$

The sulfur stoichiometric is in excess to the alkalis (a module m.s is greater than 1) which means that the SO_3 is dissolved in the clinker phases and the calcium sulphate is formed. Sulfates modulus of the samples of the group G_3 (example C_1 and C_2) is very superior to 1, so the sulfates are in the form of soluble anhydrite ($CaSO_4$) and they are dissolved in the clinker phases which avoids the false setting of these samples. Indeed, Langbeinite and Hemihydrate can create a supersaturation and they precipitates in cement matrix by causing a false setting (Eq. 7 and 8).

$$2CaSO_4K_2SO_4 \rightarrow 2Ca^{2+} + 3SO_4^{\ 2-} + 2K^+ \qquad (7)$$

$$Ca^{2+} + SO_4^{\ 2-} + 2H_2O \rightarrow CaSO_4, 2H_2O \qquad (8)$$

Rapid hardening of these two samples is probably due to the instantaneous formation of Ettringite favored by high sulphates concentrations (contributed by the clinker) and calcium which are caused by the high free lime content. An effective adjustment of the cement setting-time doesn't dependent only on optimal sulfate content, but it dependents also on the speed at the sulfate introducers components are dissolved in the mixing water. High sulfates content in the clinker impose necessarily a limit to the addition of gypsum in relation with the conformity of the SO_3 content standards in cement.

Conclusions

The study on the effect of clinker free lime on expansion, the mechanical and physical properties of cement, including compressive strength, setting time and mixing consistency, allowed us to deduce the following conclusions:

- The cement expansion increases with the clinker free lime content. The excess quantity of this product which is hydrated by Topochemical way and it creates a significant increase in the apparent volume of lime that leads to the development of the enormous pressure within the cement matrix. All that cause the increase of its expansion which results the progressive deterioration of concretes made with this cement type. This increase can also be due to small Ettringite crystals produced in high lime concentrations.
- The cement expansion decreases with grinding. It increases to 44% for cement crushed weakly, that due to slower hydration of lime which is in volume of clinker grains and there is the formation of secondary Ettringite from aluminate calcium hydrate which is hydrated later.
- The cement compressive strengths decrease with the increasing of free lime content, due to the precipitation of a high rate of Portlandite and gypsum. They increase with the grinding and the development of the reactive area.
- The mixing consistency raises for free lime rate exceeding 5%. It also depends on the presence of a large proportion of K_2SO_4 which can cause the syngenite precipitation and the increase of mixing consistency. The grinding fineness is also contributed to this increase by the multiplication of the material reactivity.
- The setting time decreases for the high contents of free lime and sulfur, due to the precipitation of gypsum.
- Adequate grinding allows the transition of the free lime in solution in the first hydration moments. The use of the Pozzolan or the fly ash as additions for the consumption of Portlandite produced by the lime hydration and the other silicates involved in other operation to avoid the adverse effects of expansion and compressive strength decrease of cementitious materials produced from clinker which present high free lime content.

References

1. Kaewmanee K.,Krammart P., Sumranwanich T., Choktaweekarn P., Tangtermsirikul S., *Constr. Build. Mater*. 38 (2013) 829-836.
2. Arnaud L., Thinet S., *Mater. Struct*.36 (2003) 355-364.
3. Charron J. P., Marchand J., Bissonnette B., *Concr. Scienc. Engin*. 3 (2001) 168-173.
4. De Schutter G., *Mater. Struct*. 35 (2002) 447-452.
5. Kada-Benameur H., Wirquin E., Duthoit B., *Cem. Concr. Res*.30 (2000) 301-305.
6. Loukili A., Chopin D., Khelidj A., Le Touzo J. Y., *Cem. Concr. Res*. 30 (2000) 915-922.
7. Mounanga P., Khelidj A., Loukili A., Baroghel-Bouny V., *Cem. Concr. Res*. 34 (2004) 255-265.
8. Pinto R. C. A., Hover K. C., *Mag. Concr. Res*. 52(2000) 345-352.
9. Roncero J., Valls S., Gettu R., *Cem. Concr. Res*. 32 (2002) 103-108.
10. Turcry P., Loukili A., Barcelo L., Casabonne J. M., *Cem. Concr. Res*. 32 (2002) 1443-1450.
11. Wirquin E., Broda, M., Duthoit, B., *Cem. Concr. Res*. 32 (2002) 1207-1213.
12. Lau O.W., Luk S. F., Cheng N. L.N., Woo H. Y., *J. Chem. Educ*. 78 (2001) 1671.
13. Nawaz A., Julnipitawong P., Krammart P., Tangtermsirikul S., *Constr. Build. Mat*. 102 (2016) 515-530
14. Tarun R. N., Canpolat F., Chun Y.M., *Cem. Concr*. 31 (2003) 525
15. Tudjono S., Purwanto X., Apsari K. T., *Proc. Eng.* 95 (2014) 426-432.
16. Abo-El-Enein S.A., El-kady G, El-SokkaryT.M., Gharieb M., *JHBRC*.11 (2015) 7-15
17. Moroccan Industrial Standards Service (SNIMA), Standard Moroccan, 2008, 3, 120.
18. Kaewmanee K., Krammart P., Sumranwanich T., Tangtermsirikul S., *Const. Build. Mater*. 38 (2013) 829-836
19. Mehta P. K., Wang S., *Cem. Conc. Res*. 12 (1982) 121-122.
20. Aardt S. H. P., Visser S., *Cem. Conc. Res*. 15 (1985) 485-494.
21. Cao H. T., Bucea L., Ray A., Yozghatlian S., *Cem. Conc. Comp*. 19 (1997) 161-171.
22. Mehta P. K., Hu F., *J. Amer. Ceram*. Soc. 61 (1978) 179-181.

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