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Predicted of hydration heat and compressive strength of limestone cement mortar with different type of superplasticizer

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Abstract. The use of some superplasticizers in the production of mortar or concrete influences the hydration kinetic and the amount of total heat. This results in a modification of some properties, namely mortar workability, mechanical strength and durability. Three superplasticizers were used; a polynaphthalenesulfonate (PNS), a melamine resin (PMS) and a polycarboxylate (PC). They have been incorporated into various amount in a standardized mortar based on limestone cement. The aim of this study was to evaluate the rheological, mechanical and Calorimeters properties of this mortar. This will select the most compatible product and more able to be used depending on the climate of the country and the cement used. The PNS is incompatible with this type of cement registering a decrease of strength but the PMS and the PC modify the kinetics of hydration with significant heat generation and improved mechanical strength. The measured heat flow is significantly influenced by the type and dosage of superplasticizer especially for low dosage. Hydration heat and compressive strength of the different mixtures can be evaluated by determining their ultimate values and ages to reach these values where the correlation coefficients are very satisfactory.

Keywords: cement; limestone; hydration heat; strength; superplasticizer; workability

1. Introduction

Addition a fine powder to cement such as limestone powder has seen extensive use in recent years in order to reduce the CO_2 emissions and enhance some properties of mortar and concrete. The use of limestone filler can enhance many aspects of cement-based systems through physical or chemical effects. Some physical effects are associated with the small size of limestone particles which can enhance the packing density of powder and reduce the interstitial void, thus decreasing entrapped water in the system.Chemical factors include the effect of limestone filler in supplying ions into the phase solution, thus modifying the kinetics of hydration and the morphology of hydration products (Yahia *et al.* 2005). The paste made from limestone cements indicates that limestone improves the clinker reactivity and the exploitation of its hydraulic potential (Tsivilis *et*

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al. 2002). It interferes during hydration of C_3A forming carboaluminates (Tikannen *et al.* 2014) and delays or impedes the ettringite-monosulfoaluminate transformation (Lothenbach *et al.* 2008). It also constitutes nucleation sites of calcium hydroxide crystals at early hydration age (Mounanga *et al.* 2011, Knapen *et al.* 2009). The increase of $Ca(OH)_2$ content in pastes of limestone cement indicates an acceleration of calcium silicates hydration, especially in cement containing 10% limestone powder (Tsivilis *et al.* 2002). Consequently, it improves the early strength but it does not have pozzolanic properties and it does not produce C-S-H (Menendez *et al.* 2001).

Furthermore the incorporation of superplasticizer to cimentituous materials is widely used but the choice of an adequate superplasticizer becomes a major preoccupation for building developers which looking to find the product giving more concrete fluidity with less adverse effect. Superplasticizers are preferred for their ability to improve the properties of concrete and give it a better mechanical behavior due to the decrease in needed w/c ratio (Puertas *et al.* 2005, Hallal *et al.* 2010). The first dispersive additives have been developed in 1930, but in 1960 the development of sulfonated melamine formaldehyde was discovered in Germany and similar derivatives of naphthalene in Japan. Then superplasticizers have begun to be used more extensively and in more controlled conditions. At the end of twentieth century, new superplasticizers based on polycarboxylates have been developed and introduced into the cement replacing the melamine and naphthalene superplasticizers. The addition of superplasticizers affects the interface between the particle surface and the pore solution and influences the physical properties such as viscosity and the yield stress of the paste (Puertas *et al.* 2005). Their dispersion effect is related to adsorption which depends on several factors such as the amount of C_3A, alkali in the clinker, the cement fineness as well as the type and dosage of calcium sulfate used to regulate the setting (Björnstrom and Chandra 2003). It was found that the traditional admixtures such as lignosulfonate and sulfonated naphthalene-type superplasticizers has high adsorption values on cement and it is supposed that the adsorption is related to the charge density and the configuration of the adsorbed molecules (Burgos-Montes *et al.* 2012). Naphtalene sulfonate formaldehyde polycondensate (NSF) superplasticizer is physically adsorbed on the surface of cement grains via electrostatic forces while polycarboxylates (PC) bearing COO^- groups interacts with cement grains through both electrostatic forces and the complexation bonding between COO^- and Ca^{2+}. The dispersing capability of PC is stronger than that of NSF. In a hydrating cement paste, PC molecules can directly adsorb on the positively charged mineral surfaces such as C_3A and Aft under electrostatic attractive forces (Zhang and Kong 2015, Zingg *et al.* 2009). In the meanwhile, the abundant Ca^{+2} ions in the pore solution may neutralize the negatively charged surfaces such as C_3S and C-S-H, and provide additional adsorption sites for anion adsorption. Thus the adsorption of PC on the negative surfaces of C_3S and C-S-H may also take place thanks to the bridging effect of Ca^{+2} ions. After the complete adsorption of the first-layer of PC on cement surface, a steadily bound outer layer of Ca^{+2} ions facilitates the second adsorption layer of PC due to the strong complexation effect of COO^- with Ca^{+2} ions (Zhang and Kong 2015) but Shin *et al.* (2008) concluded that polycarboxylates delayed the initial hydration for a long time when the chain length decreases. The strong dispersive action of these admixtures alters reaction product formation kinetics and morphology (Puertas *et al.* 2005). Their presence in mortar and concrete influences the flow, the degree of hydration and the amount of hydration products formed (Knapen *et al.* 2009).

Polymer with positive charges has a slight influence on the hydration kinetics of cement while the negatively charged polymers retard cement hydration to different extents. Carboxyl groups present a stronger retardation effect than sulfonic ones due to its larger adsorption amount and strong complexation effect with Ca^{+2}. For the comb-shaped PC co-polymers with negative charges, both the adsorption capacity and the retarding effect are stronger than those with positive charges. With the increasing molar ratio of cationic charges to anionic charges in the PC molecules, notable decrease in adsorption amount and lower retardation effect are observed in the presence of the PC co-polymers in cement paste (Zhang *et al.* 2015). On the other hand, the cements containing high dosage of C_3A consume a large amount of superplasticizer in the first minutes of hydration (Plank and Hirsch 2007). By incorporating naphthalene sulfonate to Portland cement, Zhang *et al.* (2002) found that at 3 days, hydration heat of binder pastes was not reduced in the presence of superplasticizer containing retarding component but the hydration heat liberation process was delayed. For others, (Brandstetr *et al.* 2001) the effect of melamine based superplasticizer was less pronounced, increased amount from 1% to 2% showed a gradual extension of the induction period,but no retardation in the development of the main exothermic peak which became enhanced.

The aim of this study is to test the effect of three types of superplasticizer with different nature when incorporated into limestone cement mortar formulation. The interaction of these products with this cement leads to different behaviors depending on their dosages and the properties studied. For various dosages of these admixtures, the mortars are tested in workability, compressive strength and hydration heat. Correlations are tested to better quantify their effects.

2. Experimental study

2.1 Material used

The cement used in this research is a blended cement (CEM II / 42.5) containing 10% of limestone powder. This cement is used to make a mortar based on standard sand complying with the standard NF P 15-403 (1996). The physico-chemical and mineralogical characteristics of this cement are shown in

Table 1 Three superplasticizers were used at various dosages to improve the mortar workability; the first was based on polynaphthalene sulfonates (PNS), the second was based on melamine resin (PMS) and the third was based on polycarboxylate (PC). The mass content of these superplasticizers were 40%, 40% and 30% respectively. More details of these superplasticizers are shown in Table 2. They have been diluted in the mixing water and incorporated in the mortar composition with different dosages.

Table 1 Physico-chemical and mineralogical characteristics of cement

Chemical characteristics										
Designation	PAF	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	CaO_{free}
%	4.49	21.14	5.66	3.27	62.30	0.74	1.58	0.81	0.11	0.7

Mineralogical characteristics				
Designation	C_3S	C_2S	C_3A	C_4AF
%	41.8	33.3	5.1	10.7

Physical characteristics				
Designation	Beginning of setting	End of setting	Expansion (mm)	Blain fineness (cm^2/g)
	3h5mn	5h45mn	1	3600

Table 2 Superplasticizers characteristics

Superplasticizer	Appearance	Density	Chlorine content (g/l)	PH
PNS	Liquid	1,19 ± 0,01	< 0,1	8 / 9
PMS	Liquid	1,20 ± 0,01	< 1	8.2
PC	Liquid	1,07 ± 0,01	< 0,1	6-6.5

2.2 Mortars confection

The mortars were made with cement-sand-water mass proportions of 1:3:0.5. Different dosages of each superplasticizer were added to the mixture such as 0, 0.6, 1.0 and 1.5%. The mortars were made in Hobart type mixer with a capacity of five liters, and using two different speeds (low and high). The procedure used in all tests was as follows: dry cement and sand were firstly mixed at low speed for 1 minute and 2/3 part of mixing water were added and the mixture was also mixed at low speed for 1 minute, third part of mixing water and superplasticizer were added and the mixture was mixed for the third minute at low speed. Finally the mixture was mixed for one more minute at high speed.

2.3 Testing method

Flow table test according to standard ASTM C230-83 (1983) was used to measure the workability of each mixture after mixing. Mortar was placed in a truncated mold on the shaking table when it received 15 shots in 15 seconds after demolding. The spread mortar diameter was measured and the workability of the mortar was deduced. Spread was calculated as the ratio between the increases in diameter to the initial diameter of the mortar mold.

Prismatic mortar specimens having 40x40 mm dimensions were prepared for compressive strength study. Specimens were cast in steel moulds and kept in a moist room at 20°C. Demolding took place one day after and specimens were retuned in the moist room until the day of testing. Compressive strength was determined at the age of 1, 3, 7, 28 and 90 days according to EN 196-1 (1987).

Hydration heat test was carried out according to NF 15-436 (1988) standard. The method is based on the Langavant Calorimeter. This semi-adiabatic method consists to quantify the heat generated during cement hydration using a thermally isolated bottle. Since the exterior conditions are very influential, the test was carried out at a constant temperature of 20±2°C. The temperature measurements were made up to 5 days, since the heat increase was observed to be very low at later ages. The temperature results were used to calculate the hydration heat developed by the test sample. The hydration heat of the mortar is the combination of the accumulated heat in the calorimeter and the heat dispersed in the environment. At time *t*, the hydration heat *q* by gram of cement is obtained by the Eq. (1).

$$q = \frac{C}{m_c}\,\Delta\theta + \frac{1}{\mathrm{m_c}}\int_{o}^{t} \alpha\,\Delta\theta\,\mathrm{dt} \qquad (1)$$

Where C is the total thermal capacity of the apparatus (J/°C), m_c is the cement mass (g), $\Delta\theta$ is the mortar heating difference to the ambient temperature (°C), and α is the total calorimeter thermal loss coefficient (J/h/°C).

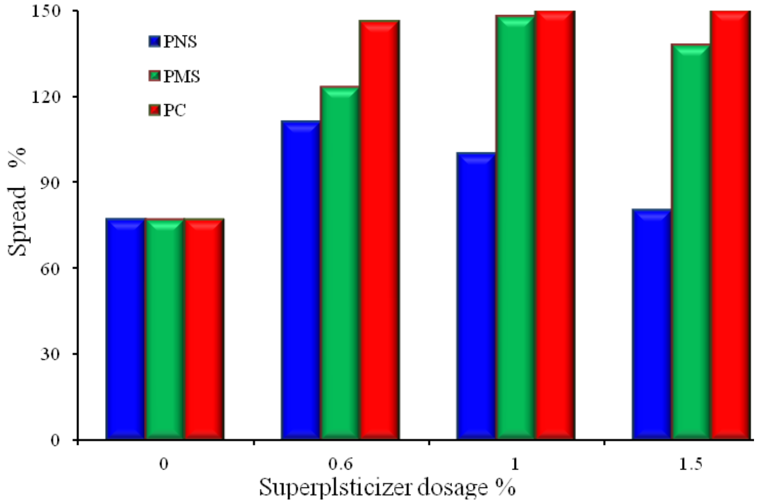

Fig. 1 Influence of dosage and type of superplasticizer on the mortar spreading

3. Result and discussion

3.1 Workability

The workability results of all mortars measured by the flow table are presented in Fig. 1. It is clear that the addition of superplasticizer increases the fluidity of all mortars studied. For PNS superplasticizer, an increase in the dosage improves the workability of the mortar until a dosage of 0.6%, beyond this value the increase of superplasticizer dosage leads to a deterioration of the workability but stills better than that of no-adjuvanted mortar. From this, it can be concluded the negative effect of excessive dosage of PNS with limestone cement. For PMS superplasticizer, an optimum value of the flow is observed for a dosage of 1% and decreases from 148% to 138% when the dosage reaches 1.5%. This result shows a slight loss of the efficiency at high amounts of PMS. On the other hand, the mortar with PC superplasticizer has a very high workability which reaches 146% with just a 0.6% dosage. For higher amount, workability remains significant and immeasurable by the shock table with a spread exceeding 150%. This indicates high compatibility between polycarboxylate and limestone cement.

Some studies, (Puertas *et al.* 2005) have shown, from the analysis of pore water, than the rich cements in C_3A consume many additional polymers superplasticizer in the first minutes of hydration. The high demand for PNS observed for the cement used is probably due to the high C_3A content (5.1%), which makes it incompatible. On the other hand the presence of limestone powder (10%) in cement contributes to accelerating the hydration of tricalcium aluminate and the ettringite formation accompanied by a decrease in fluidity. This confirms the results of other studies on limestone cement where the blended cements require more superplasticizer for a given spreading (Björnstrom and Chandra 2003). Unlike, the other types of superplasticizer (PMS and PC) give an acceptable mortar workability at moderate dosages.This efficiency can be attributed to their chemical nature formed from long molecular chains that make possible to cover completely the cement particles and ensure a high dispersion. This is in conformity with other results (Burgos-Montes *et al.* 2012, Adjoudj *et al.* 2014) which showed that the superplasticizers polymer made

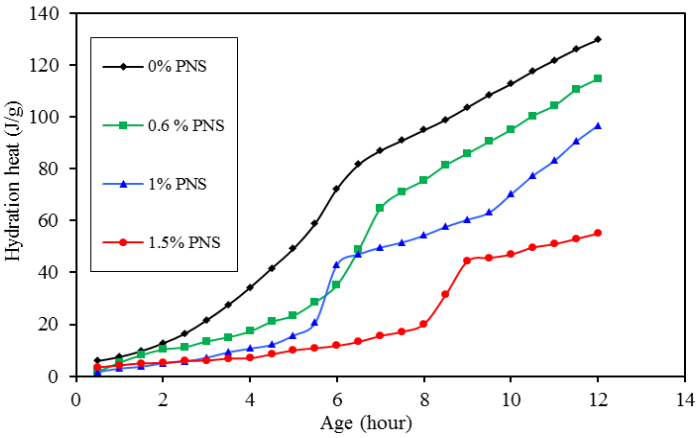

Fig. 2 Evolution of hydration heat of cement at early age containing different dosages of PNS

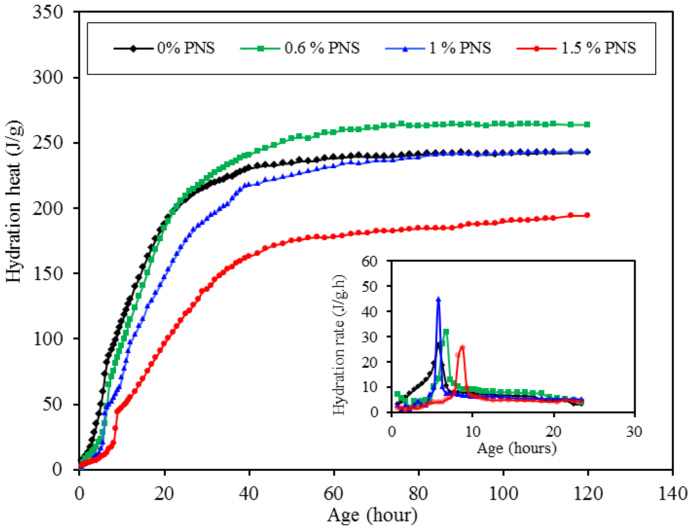

Fig. 3 Evolution of hydration heat and rate of hydration of cement with different dosages of PNS

with longer chains have higher dispersion possibilities. In addition Shin *et al.* (2008) concluded that polycarboxylates retard the hydration reaction when the chain length decreases with increasing molecular weight. Other study (Zhang *et al*. 2016) showed that the absolute values of zeta potential of mortars increased with the increase of superplasticizer content which can explained the fluidity and the fluidity loss of the mixtures.

3.2 Hydration heat

Fig. 2 shows the quantity of hydration heat released by limestone cement mortar superplasticized with different dosages of PNS. It is observed since the early hours of hydration that the control mortar releases more heat than all adjuvanted samples. At later age, low PNS dosages superplasticizer release more water, promote hydration grains and produce more hydration

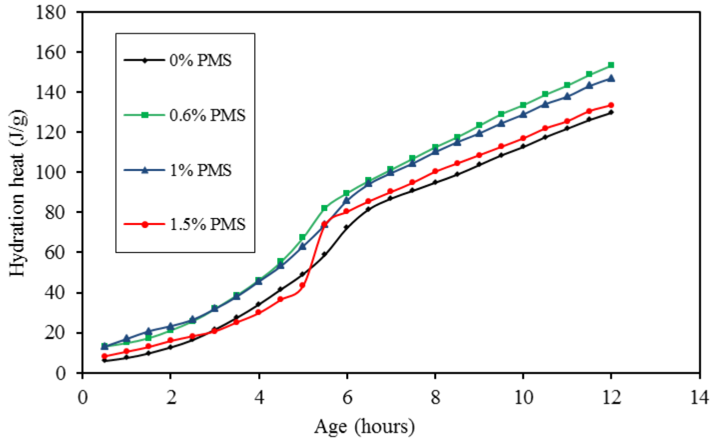

Fig. 4 Evolution of hydration heat of mortar at early age containing different dosages of PMS

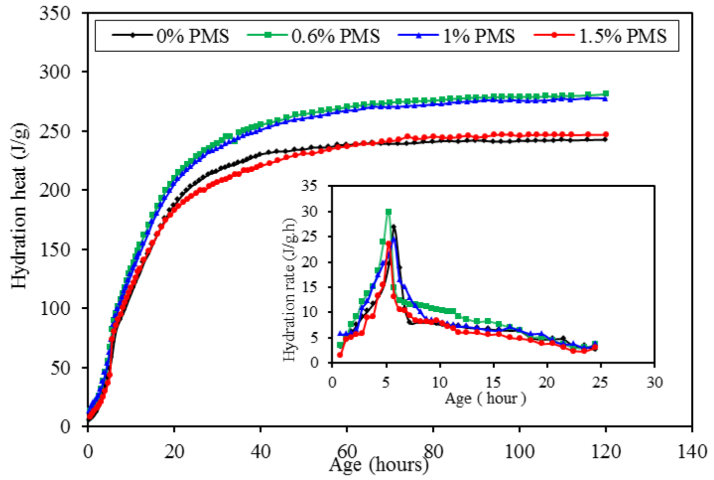

Fig. 5 Evolution of hydration heat and rate of hydration of cement with different dosages of PMS

heat. As shown in Fig. 3, mortar mixing with 0.6% of superplasticizer releases high value of hydration heat that reaches 264 J/g while that without admixture releases low value of 242 J/g. For high dosage of superplasticizer the hydration heat decreases to 194 J/g. High amounts of PNS superplasticizer delay the contact of the cement particles with mixing water and cause a decrease of the total heat. This notable decline confirms the efficiency loss of this superplasticizer for high dosages.The appearance of the principal peak is observed at 5.7 hours for the control mortar with a magnitude of 26.7 J/g.h which increases by increasing the dosage of PNS until 45 J/g.h and its appearance was recorded at 6 hours for 1%. Over this dosage, flow value decreases and the dormant period is extended as illustrated in Fig. 3. From this result, it can be concluded that the PNS superplasticizer based on naphthalene sulphonates plays a significant role as a setting retarder. This finding is compatible with Kadri and Duval (2009) results in which the addition of 0.6% to 5.5% naphthalene sulphonates to cement mortar extends the dormant period from 2 to 14 hours followed by a reduction of the exothermic peak. Similarly, Pirazzoli *et al.* (2005) found that

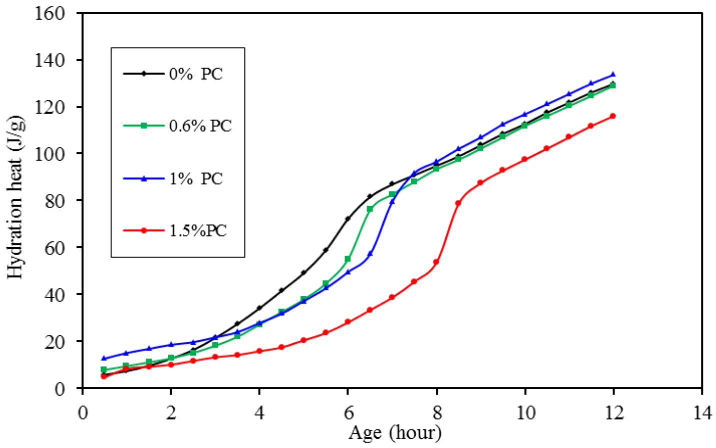

Fig. 6 Evolution of hydration heat of mortar at early age containing different dosages of PC

the addition of PNS to the C_3S paste increases the dormant period and reduces the length of the acceleration period.

During the first 12 hours of hydration, Fig. 4 shows that the addition of Melamine resin (PMS) results in an acceleration of the hydration heat such that 153 J/g is obtained for a dosage of 0.6% against 130 J/g of the control mortar. For higher dosages, the heat released for the corresponding mortars begins to decline but remains higher than that of the control mortar. After five days of hydration, Fig. 5 shows that the addition of Melamine resin (PMS) at different dosages to limestone cement mortar increases the heat quantity released for all ages compared to cement control, more significantly for low dosages. The heat registered is 242, 281, 277 and 247 J/g for the control mortar and those containing 0.6%, 1%, and 1.5% of PMS respectively. This indicates the effectiveness of this admixture where it is used at an optimal dosage ranging from 0.6% to 1%. Hydration rate curves illustrated in Fig. 5 are nearly overlaid and differ only by their amplitudes. The value of the peak of hydration rate increases from 26 J/g.h for control mortar to 30 J/g.h for mortar adjuvanted with 0.6% of PMS with an acceleration of half hour. For mortars containing high dosages, the peak of hydration rate decreases and keeps the same kinetics as that of a mortar without admixtures. From this, it is clear that the PMS has a weak effect on the setting and the hydration kinetics. This is aligned with Brandstetr *et al.* (2001) results, where increasing dosage of melamine from 1% to 2% in ordinary Portland cement induces a gradual extending of the dormant period without delaying the exothermic peak.

The amount of the hydration heat released for mortar containing different dosage of PC is illustrated in Figs. 6 and 7. After mixing, the control mortar generates more heat than the others mortars adjuvanted with different polycarboxylate dosage. Just a few hours later, the heat curves converge to the same value for all mortars except for that containing an excessive dosage of 1.5%. At later age, the hydration heat of all superplasticized mortars is greater than that given by the control mortar, this value changes from 242 J/g for control mortar to 265, 251, 250 J/g for a dosage of 0.6%, 1%, and 1.5% of PC respectively. By adding polycarboxylate (PC) to cement, the appearance of the peaks of hydration rate is delayed and its magnitude reaches 50 J/g.h at 8.25 hours for 1.5% of PC as shown in Fig. 7. This result is consistent with the work of several researchers (Puertas *et al.* 2005). In addition, Shin *et al.* (2008) claimed that polycarboxylates delay the initial hydration of cement. It can be clearly noted that others results found by Zhao *et al.*

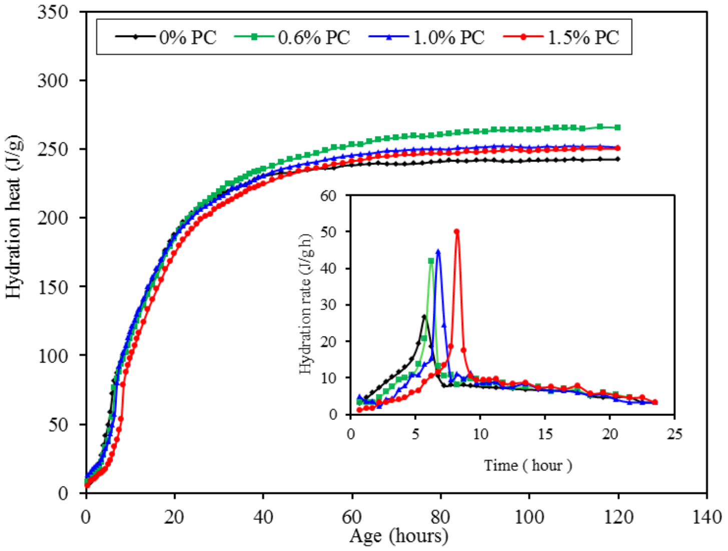

Fig. 7 Evolution of hydration heat and rate of hydration of cement with different dosages of PC

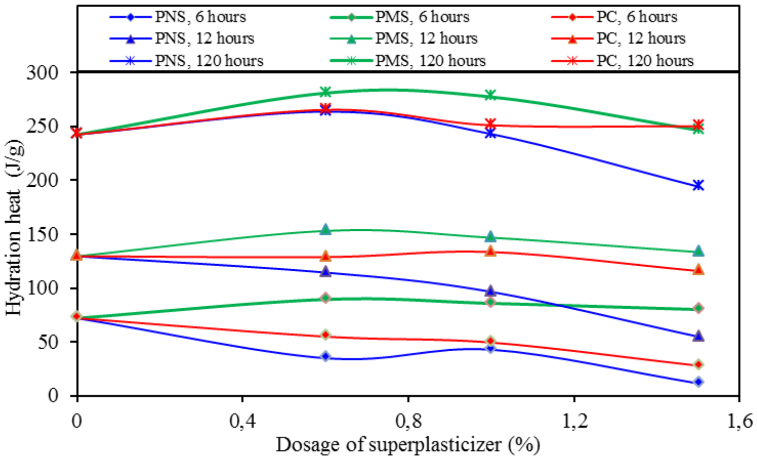

Fig. 8 Influence of type and superplasticizer dosages on the hydration heat of mortar

(2017), also observed that in cement sample containing PC superplasticizer, the time to reach the maximum exothermic rate is longer compared with cement sample without PC. This is mainly attributed to the interaction between PC molecules and Ca^{2+}, leading to the lower Ca^{2+} concentration in the system that hinders the solid phase hydration (Uchicawa *et al.* 1997, Anagnostopoulos 2014). Similarly, Zingg *et al.* (2009) concluded that the heat flow is more delayed and the dormant period is extended in presence of a short molecular chain and high density of polycarboxylate.

Fig. 8 illustrates a comparison of the hydration heats released at different ages from which it is clear that the PNS represents the weak active superplasticizer particularly at early age. When it is incorporated at different dosages, the mortar containing 1% of PNS exhibits a heat drop which reaches 40% and 20% after 6 and 12 hours respectively. At 120 hours, the effect of this fall

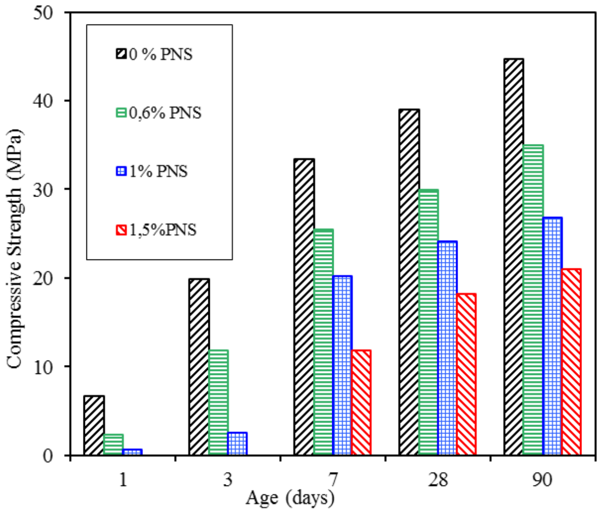

Fig. 9 Variation of compressive strength mortars with different dosages of PNS

disappears and becomes significant only beyond 1% dosage. The superplasticizer based on PMS is very active and its presence attributes a high activity to cement grains hydration which confers a greater heat released even for high dosages. This cement reactivity is more evident at early age and for low dosages. For low PMS presence of 0.6%, a 24%, 18% and 15% increase in heat is observed at 6, 12 and 120 hours respectively. When the dosage increases to 1.5%, the heat increase is only 11%, 3% and 1% for the same ages. The low effect of the superplasticizer based on polycarboxylate is well obvious on the results presented in Fig. 8. Its presence at moderate dosage contributes only from 3 to 10% increase in the heat released while its high dosage acts negatively on hydration at early age and becomes with no effect at later ages.

3.3 Compressive strength

Fig. 9 shows the variation of the compressive strength according to the PNS superplasticizer dosage. It is clear that the value of the control mortar compressive strength is much higher than that of the samples with superplasticizer for all ages. At 1 day, the compressive strength of the superplasticized cement mortar is practically negligible. Identical results were found (Yousuf *et al.* 2017) where the strength decreases in the presence of an excessive dosage of the superplasticiser and the paste lacks the sufficient strength to sustain the load at 1 day. On the other hand, an increase in the PNS dosage from 0.6% to 1.5% reduces the 90 days compressive strength from 35 MPa to 21 MPa. The maximum value, with this superplasticizer, remains 10 MPa lower than that of the control mortar. This result confirms the incompatibility of this admixture with limestone cement compound which resulted in a decrease of workability when the dosage exceeds 0.6%. Also, the results found by Pirrazoli *et al.* (2005) concluded that the hydration of cement paste adjuvanted with PNS superplasticizer has hydration products with a small volume compared to the products hydration of no superplasticized cement.

From Fig. 10, it will be noted that the values of compressive strength recorded for mortars adjuvanted by 0.6% and 1% PMS are closed to those given by the control mortar at all ages and tend to be improved at long-term. At 90 days, a decrease of mortar compressive strength is only

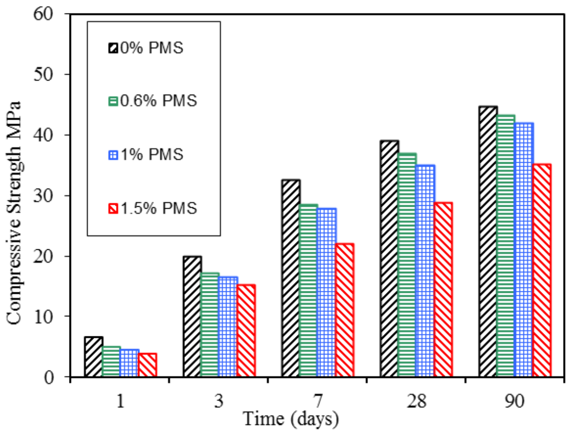

Fig. 10 Variation of compressive strength mortars with different dosages of PMS

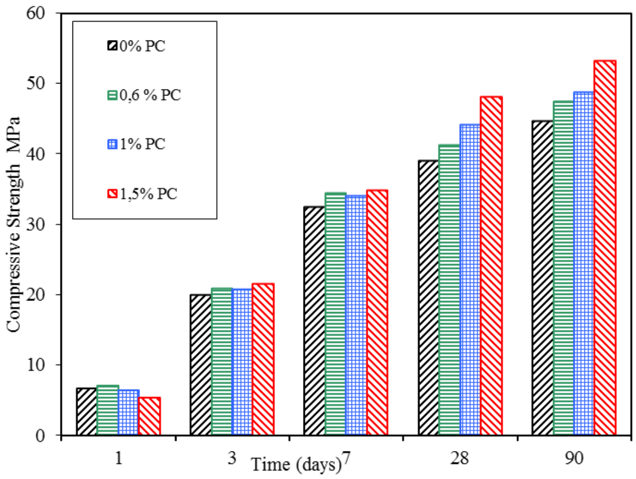

Fig. 11 Variation of compressive strength mortars with different dosages of PC

4% and 6% for mortar adjuvanted with 0.6% and 1% of PMS. However for high dosage of 1.5%, the strength drop reaches 21%. This may be the consequence of the workability improvement observed in this dosage range. This is in conformity with Brandstetr *et al.* (2001) results where the efficiency of the melamine resin-based superplasticizer is observed at low concentrations (<1%) and the high strength is obtained with just a 0.5% dosage.

Fig. 11 illustrates the variation of the compressive strength as a function of the polycarboxylate dosage. The incorporation of polycarboxylate (PC) to cement mortar improves the workability and the compressive strength of mortar at all ages tested. At three days, the compressive strengths of mortars superplasticized with 0.6%, 1% and 1.5% of PC increase by 5%, 4% and 8% respectively. This increase improves during hydration and reaches 6%, 13% and 23% at 28 days. This indicates a high compatibility of polycarboxylate (PC) with this type of cement. This is in conformity with Puertas *et al.* (2005) results, where the use of superplasticizer based on polycarboxylate at low concentrations improves the compressive strength by reducing the porosity of the paste. This strength can reach higher values than those obtained for a control mortar.

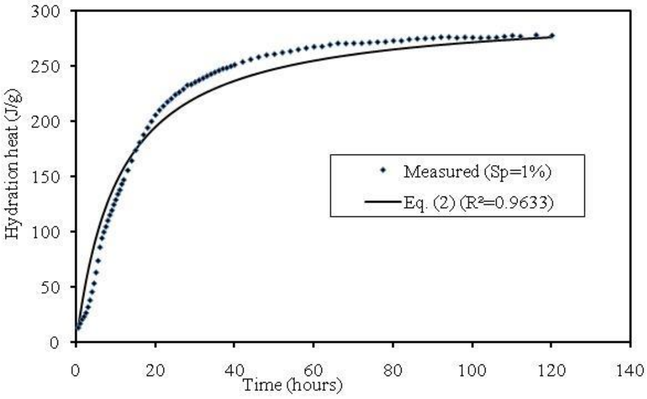

Fig. 12 Variation of measured hydration heat and predicted with Eq. (2) for mortar with 1% of PMS superplasticizer

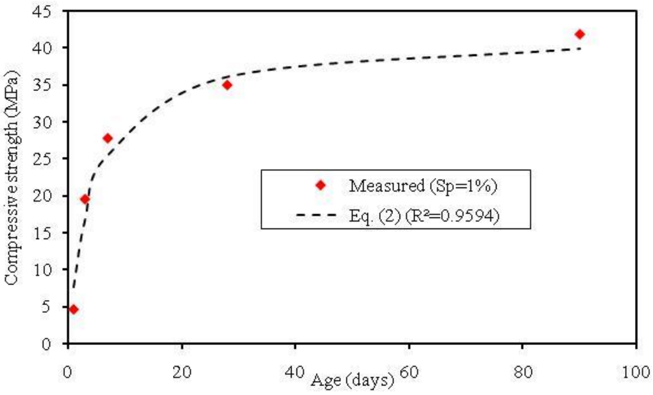

Fig. 13 Variation of measured compressive strength and predicted with Eq. (2) for mortar with 1% of PNS superplasticizer

4. Result correlation

To analyze the obtained results, an approach recommended by ASTM C1074-93 (1993) to analyze some concrete properties development under isothermal curing was used. It was assumed that the kinetics of the concrete properties at a constant temperature can be represented by the following hyperbolic equation.

$$X(t) = X_u \frac{t - t_0}{(t - t_0) + t_{50}} \tag{2}$$

Where $X(t)$ is the concrete property at tage; X_u is the ultimate property value at long term; t_0 is the age when the concrete property development is assumed to start and can be assumed to zero for hydration heat and compressive strength, and t_{50} is the age where the concrete property reaches 50% of its ultimate value. A least-squares regression analysis for Eq. (2) was used to determine the best-fit values of X_u and t_{50} for each set of data (Eren 2002, Ezziane *et al.* 2010). The correlation of the results of compressive strength and hydration heat by linear regression gives the values of the

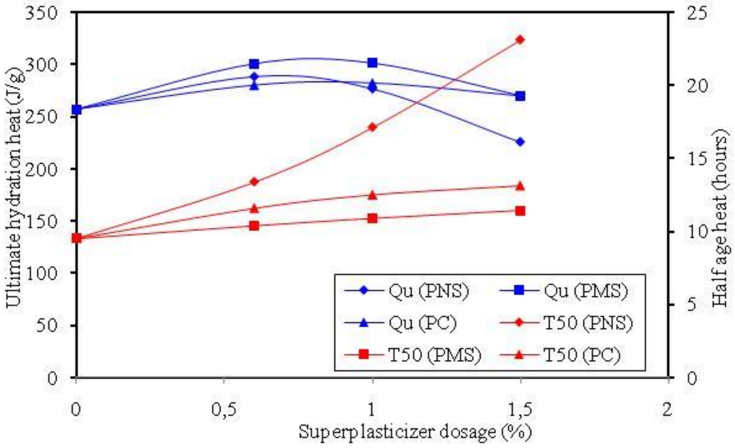

Fig. 14 Ultimate hydration heat and half age heat according to superplasticizer dosage

age t_{50} and the ultimate property values X_u for each mixture. Curves drawn in Figs. 12 and 13 are representative samples for the resulting best-fit hyperbolic curves. It is seen that Eq. (2) fits the data quite well with an accurate coefficient of correlation.

From these results, it is clear that Eq. (2) overestimates the ultimate values. For this reason, the correlation of the test results is carried out by first looking for the ultimate values of compressive strength with only the results beyond 7 days and hydration heat with only the values recorded after 24 hours. The values of the half age t_{50} will be deduced from all the values by fixing the ultimate values of compressive strength and hydration heat firstly found. All values found, of ultimate values and half ages of several mixtures, are illustrated in Figs. 14 and 15.

From the results presented in Fig. 14, it is clear that each superplasticizer causes a delay in the hydration development. The t_{50} ages increase linearly with the increase of the PMS and PC dosage whereas for the PNS this variation takes a polynomial form and the delaying effect is more important. For a 1% dosage, the age to reach half of the final hydration heat is 17.1, 10.8 and 12.5 hours for the PNS, PMS and PC respectively. The ultimate hydration heat released during the cement hydration is very affected by the dosage and the superplasticizer type. These ultimate values change takes a polynomial form according to each superplasticizer dosage. The PNS effect is optimal for a dosage of 0.6% where the final heat improves by 12% while for high dosages of 1.5% a considerable drop is observed. The presence of PMS and PC gives an additional hydration heat release compared to control mortar for all dosages used. With a 1% dosage, the final hydration heat increases by 17% and 9% for mortar mixed with PMS and PC superplasticizer respectively. In the same way Mehdipour *et al.* (2017) concluded that limestone cement mixed with PC superplasticizer exhibits larger extent of hydration kinetics as indicated by higher magnitude of heat at main hydration peak.

The ultimate compressive strength obtained for each mortar as well as their kinetics described by the half-strength age are shown in Fig. 15. From these results, the effect of each superplasticizer is illustrated. As reported by Zhang *et al.* (2016), the compressive strength at late stage (28 days) was slightly influenced by the dosages and the type of superplasticizers. The PNS appears to have a negative effect on ultimate strength where the fall is proportional to the dosage used. The PMS retains a neutral effect up to a dosage of 0.6%, beyond its presence weakens the mortar strength. The ultimate strengths are greatly improved with the presence of the PC such that an increase of

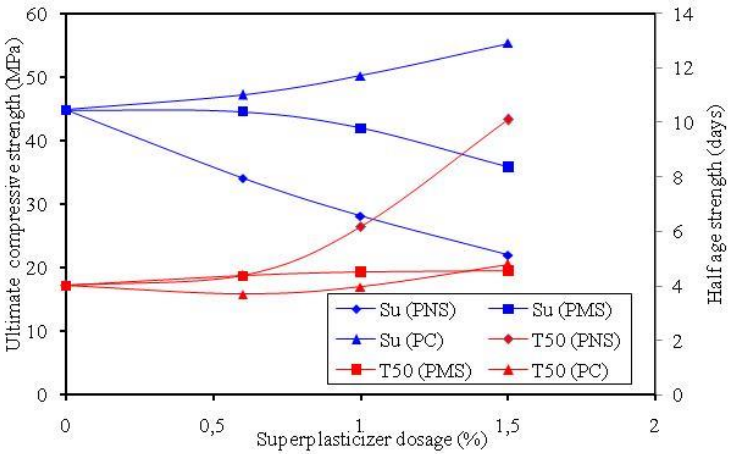

Fig. 15 Ultimate compressive strength and half age strength according to superplasticizer dosage

Table 3 Eqs. (3)-(4) parameters found for each superplasticizer type.

Parameters of Eq. (2)	a_1	b_1	c_1	a_2	b_2	c_2
	Ultimate hydration heat (Q_u)			Half hydration heat age (t_{50}, hours)		
PNS	-78,13	97,44	256,5	3,59	3,92	9,50
PMS	-71,10	115,32	256,50	-0,15	1,44	9,50
PC	-33,81	59,55	256,50	-1,11	4,05	9,50
	Ultimate Compressive strength (S_u)			Half strength age (t_{50}, hours)		
PNS	2	-17	46.4	4	-0.1	3.92
PMS	-6	2.6	46.4	-2	2.5	3.92
PC	3	2.3	46.4	0.7	-0.26	3.92

5%, 12% and 23% is recorded when the mortar is mixed with 0.6%, 1% and 1.5% superplasticizer respectively. The development of compressive strengths is the combined result of the hydration products and the microstructure quality of the cement paste. Although the PNS has a favorable effect on hydration heat for low dosages, it causes a great degradation of porosity which reduces the compressive strength of mortar.

In order to better consider the superplasticizer effect on the parameters of Eq. (2), several relationships have been tested to express the X_u and t_{50} variation and the polynomial form has shown a high degree of satisfaction, from which the values X_u and t_{50} were expressed as follows

$$X_u = a_1 S_p^2 + b_1 S_p + c_1 \tag{3}$$

$$t_{50} = a_2 S_p^2 + b_2 S_p + c_2 \tag{4}$$

Where a_1, b_1, c_1, a_2, b_2 and c_2 are coefficients that will be determined by fitting test results for each properties and each superplasticizer. S_p is the superplasticizer dosage expressed as the ratio of the weight of the superplasticizer to that of the cement. Table 3 summarized the values of Eqs. (3)-(4) parameters found by regression analysis of the test data.

From Eq. (2)-(3) and using the parameters shown in Table 3, the ultimate values of the half-age can be directly determined for each type of mortar. Figs. 16 and 18 illustrate the variation of

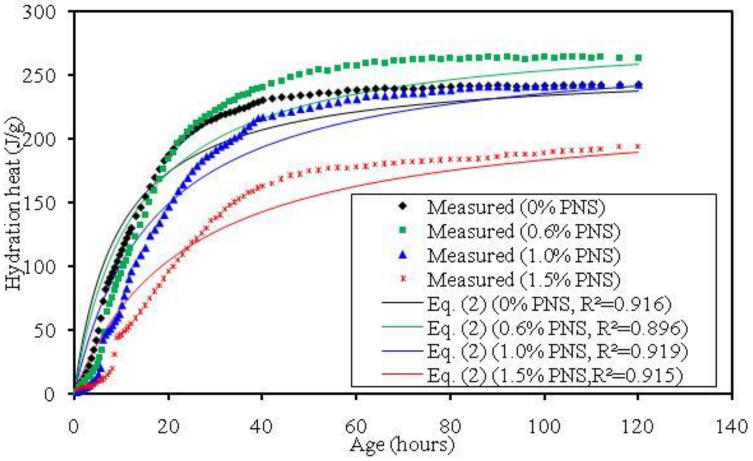

Fig. 16 Evolution of measured and predicted hydration heat for PNS superplasticized mortar

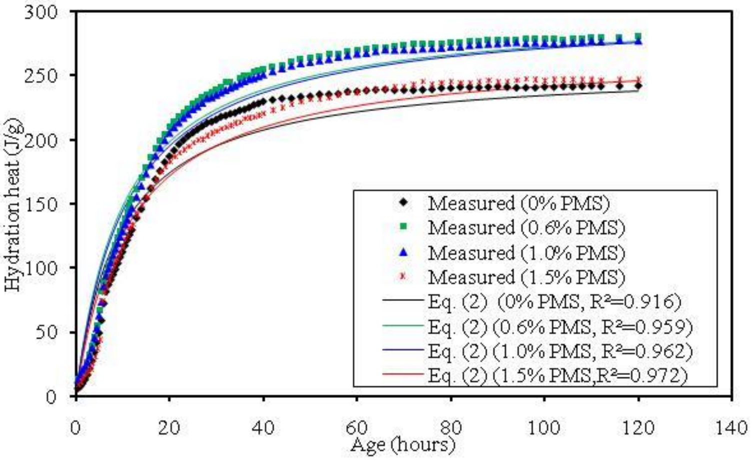

Fig. 17 Evolution of measured and predicted hydration heat for PMS superplasticized mortar

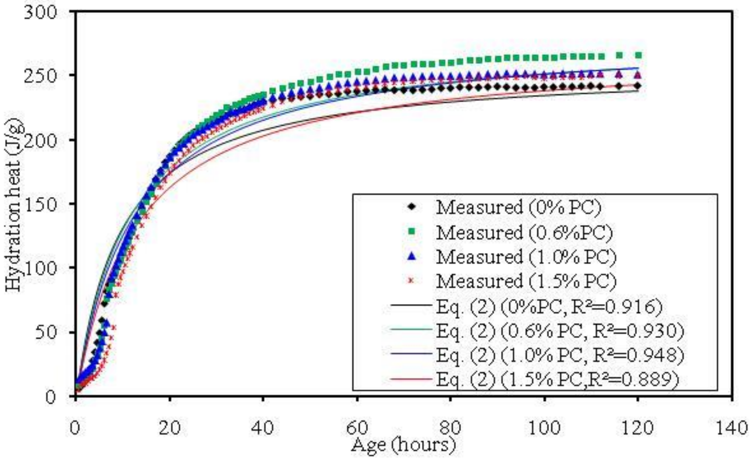

Fig. 18 Evolution of measured and predicted hydration heat for PC superplasticized mortar

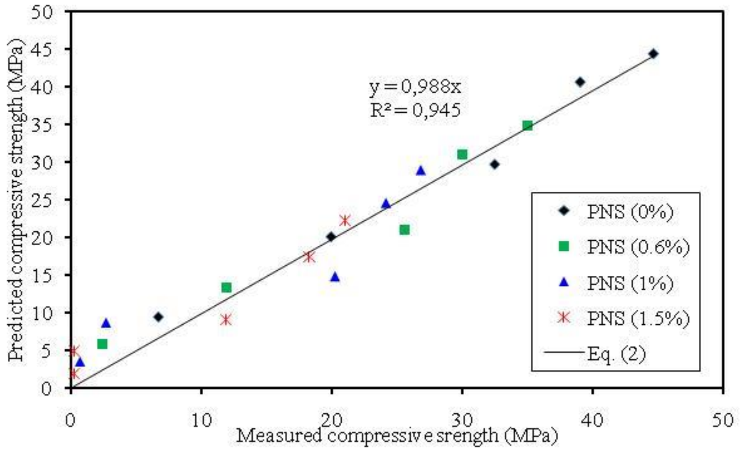

Fig. 19 Comparison of measured and predicted compressive strength PNS superplasticized mortar

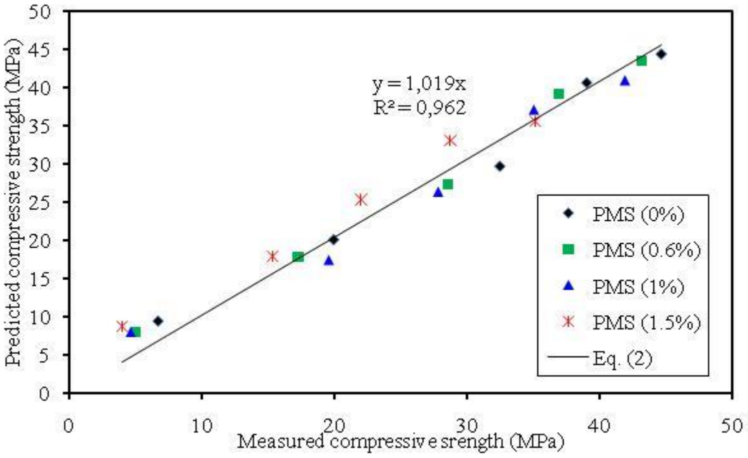

Fig. 20 Comparison of measured and predicted compressive strength PMS superplasticized mortar

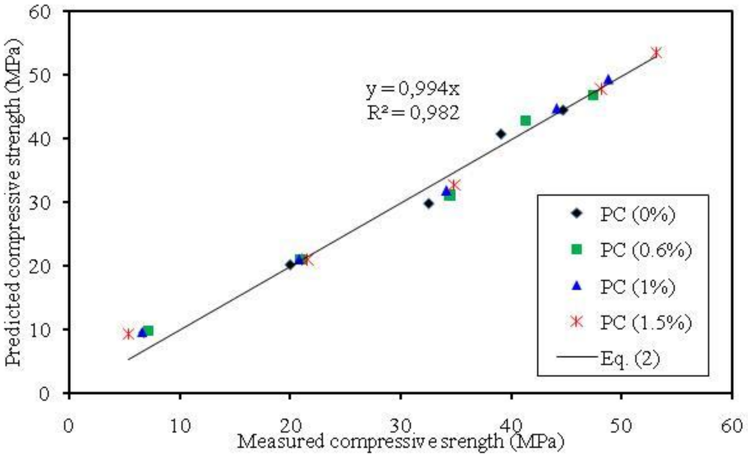

Fig. 21 Comparison of measured and predicted compressive strength PC superplasticized mortar

hydration heat measured and calculated by Eq. (2) for different dosages of each superplasticizer used. According to these results, high correlations with coefficients close to unity are observed. The hydration heats predicted by this relationship are more suitable for PMS and PC superplasticizers and for superplasticizer content around the saturation dosage (1%). By following the same procedure, compressive strengths for the different mortars are determined. Figs. 19-21 illustrate a comparison of the results of compressive strength measured and calculated by Eq. (2). The obtained results are encouraging and testify to the reliability of the relationship 2 to predict the compressive strength evolution.

5. Conclusions

Based on an experimental study conducted for the superplasticizer type effect on compressive strength and hydration heat the following conclusions can be drawn.

- It is obvious that the type of superplasticizer with cement type, strongly influence the effectiveness and the compatibility of the mixture. As can be noted that the fluidity of PC is larger than that of PMS and PNS whatever the dosage used.
- Limestone cement has a high workability when mixed with 0.6% PNS or 1% PMS, while polycarboxylate (PC) may be most compatible with this type of cement and more efficient to improve the fluidity of the paste at dosages used.
- The PNS effect is optimal for a dosage of 0.6% where the final hydration heat improves by 12% while for high dosages of 1.5% a considerable drop is observed. The presence of PMS and PC gives an additional hydration heat release compared to control mortar for all dosages used. With a 1% dosage, the final hydration heat increases by 17 and 9% for mortar mixed with PMS and PC superplasticizer respectively.
- Low dosage of PNS promotes hydration of grains and produces more hydration heat but higher dosages delays the contact of cement particles with mixing water and causes a decrease in the final heat released.
- Incorporation of the Polymelamine resin (PMS) reduces the heat flow compared to control mortar without changing the time of its occurrence. So, PMS has no effect on the setting and the hydration kinetics of limestone cement.
- The hydration heat of all mortars adjuvanted by Polycarboxylate (PC) is higher than of the control mortar for all ages. The increase of superplasticizer dosage delays the initial cement hydration, increases the heat flow and delays the dormant period.
- For compressive strength, the polynaphthalenesulfonate (PNS) is incompatible with this type of cement and causes strength loss. But the addition of the melamine resin (PMS) at low dosages (0.6%) improves the strength despite that remains lower than that of control mortar. However the incorporation of Polycarboxylate (PC) greatly increases compressive strength which may reach values higher than the control cement.
- Eq. (2) is a very suitable means for estimating the ultimate values and the kinetics of cement properties. These parameters take polynomial forms according to each superplasticizer dosages. The correlation coefficients found for hydration heat and compressive strength are close to unity.

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