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Coupled effect of time and temperature on variations of yield value of highly flowable mortar

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Abstract

In order to enhance the performance of self-consolidating concrete, it is important to have a better understanding of the rheological behavior of the material. The initial rheological parameters and their variations with time are closely affected by material temperature, type and dosage of high range water-reducing admixture (HRWRA), and elapsed time. This paper presents the results of an investigation aimed at evaluating the coupled influence of time and temperature on the variations of yield value with time of mortars made with two types of HRWRA: polynaphtalene sulfonate and polycarboxylate polymer. Four mortars extracted from self-consolidating concrete mixtures proportioned with various binder types and with water-to-binder ratios of 0.42 and 0.53 were prepared at 10 to 30 °C.

Test results show that the yield value varies linearly with the coupled effect of time and temperature during the dormant period for mixtures made with polynaphtalene sulfonate-based HRWRA. However, such changes are found to depend on the mixture temperature for mixtures made with polycarboxylate-based HRWRA, which can influence the dispersion efficiency of the polycarboxylate polymer. The threshold temperature of mixtures made with PCP–HRWRA is shown to vary with mixture composition. Below a given threshold temperature, the mortar exhibits a considerable degree of retention or even reduction in yield value over 30% of the dormant period. A sharp increase in yield value is observed beyond 30% of the dormant period. Above this threshold temperature, the yield value is shown to increase linearly with time.

Keywords: Temperature; Fresh concrete; High range water reducers; Rheology; Calorimetry

1. Introduction

The use of high range water-reducing admixture (HRWRA) is effective in enhancing the workability of cement-based materials. Such water-soluble organic polymers can enhance flowability of cement paste by dispersing the cement particles into the interstitial solution, thus reducing the inter-particle friction among cement grains and decreasing the degree of water entrapment among flocculated particles. The benefit of using polynaphtalene sulfonate (PNS), polymelamine sulfonate (PMS), and more recently polycarboxylate polymers (PCP) as HRWRA to enhance workability of cement-based systems is well established. However, depending on the characteristics of the binder system and the HRWRA, incompatibility problems lead to particularly high demand of the admixture or excessive loss of fluidity with time. Such cement–HRWRA incompatibility can involve an interaction between the sulfonate groups within the hydration reaction and the cementitious ionic matrix [1]. Long-chain polymers, with significant molecular weights, have been developed more recently to improve the dispersion of cement particles through a more effective steric effect mechanism. Polycarboxylate polymers constitute a family of these newly used admixtures that are highly effective in enhancing concrete workability and its retention with time. These advantages are especially noticeable in mixtures made with low water-to-binder ratios (W/B), given the superior dispersing ability of the PCP polymer compared to PNS– or PMS–HRWRA that can exhibit sharper drops in fluidity with time [2].

It has been shown that the efficiency of PCP–HRWRA in decreasing the water demand in cement paste is affected by the mixture composition and mixing procedure [3,4]. A relatively

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high concentration of sulfate ion in the interstitial solution can lead to incompatibility between the binder and HRWRA, thus affecting the adsorption behavior of the PCP onto cement particles [5,6].

The interaction of cement with other admixtures, such as viscosity-enhancing agents (VEA) and HRWRA, can lead to loss in fluidity or delay in set time, depending on the concentrations of either admixture [7]. Temperature also affects the level of incompatibility between the cementitious materials and various admixtures.

Golaszewki and Szwabowski [8] reported that the rheological properties of mortar mixtures made with PNS–HRWRA are strongly influenced by temperature. An increase in mixture temperature can lead to an increase in yield value and a decrease in plastic viscosity. For mortars prepared at a W/B of 0.40 and an HRWRA dosage of 2.25%, by mass of binder, and a W/B of 0.50 and 1% HRWRA, the increase in temperature of 10 to 40 °C is shown to result in a higher rate of increase of τ_0 with time, and is different according to type of binder systems. Similar results were found on mortars prepared with a W/B of 0.42 to 0.53 and either PNS or PMS HRWRA at dosage rates ranging between 0.28% and 0.8%, by mass of binder [9]. The increase in mixture temperature from 10 to 30 °C resulted in a linear increase in yield value with time. A decrease in the temperature of the mortar resulted in reducing the rate of cement hydration, thus lengthening the duration of the dormant period [10]. The evolution of yield value with the elapsed time (t) at various temperatures can then be expressed as follows:

$$\tau_0(t) = \tau_0(0,T) + \Delta\tau_0 t \qquad (1)$$

where $\tau_0(0)$ refers to the initial yield stress, and $\Delta\tau_0$ corresponds to the increase of yield stress with the elapsed time. The variation of $\Delta\tau_0$ with reciprocal temperature ($1/T$) can be expressed as:

$$\Delta\tau_0 = \alpha e^{-\beta/T} \qquad (2)$$

where α and β are experimental constants that can be deducted from the regression results in a $\Delta\tau_0$ with reciprocal temperature chart. Consequently, the evolution of yield value with temperature (T) and the elapsed time (t) can then be expressed as follows

$$\tau_0(t) = \tau_0(0,T) + \alpha e^{\beta/T} t \qquad (3)$$

The τ_0(0,T) refers to the initial yield value at a given temperature T, $\Delta\tau_{eq}$ is the rate of increase of yield value with normalized or relative time as defined by Ref. [9], and α, and β are experimental constants that depend on the mixture proportioning [10]. The same trend was observed for mortar mixtures made with PCP–HRWRA; however, these mixtures had a lower rate of increase in τ_0 with time over a 2-h test period than those prepared with PNS–HRWRA, regardless of the temperature of the mixture [8].

Changes in rheological properties with time can be due to physical factors (coagulation and restructuring of the microstructure) and chemical factors (cement hydration and reduction in free water content). Key factors affecting changes in rheological properties with time include temperature, mixture composition, and the interaction between the binder and HRWRA in use. The influence of temperature on hydration kinetics and setting of cement is well documented [5,11,12]. Changes in temperature can influence the rheology of the cement paste through various mechanisms, such as the rate of adsorption of HRWRA [1]. The concentration of the residual HRWRA has a direct effect on the rheology of the paste and the hydration kinetics of the cement. For example, Jolicoeur et al. [1] showed that the concentration of adsorbed PNS–HRWRA and the residual polymer remaining in the aqueous phase can vary with paste temperature. This can have direct implication on rheological properties. The influence of temperature on the rheology of cement-based materials made with PCP–HRWRA is not well documented.

2. Investigations

2.1. Research significance

Limited data are available on the coupled effect of HRWRA type and temperature on variations of rheological parameters over the dormant period of cement hydration of cement based materials. The study reported herein seeks to evaluate the coupled effect of temperature and time on variations of yield value (τ_0) with time for mortars derived from SCC mixtures made with PNS– and PCP–HRWRA. Such data are necessary to understand some of the mechanisms affecting workability retention of SCC over extended periods of time, which can be well into the dormant period of cement hydration. Understanding changes in rheology during the dormant period of cement hydration is critical for handling, delivery, and placement operations of the concrete and subsequent characteristics of the plastic concrete, such as segregation and variations in formwork pressure with time. The study also establishes a technique to evaluate the influence of the coupled effect of time and temperature on the variations of rheological properties over extended periods of time. This can be of special interest to concrete technologists and materials suppliers for the development and testing of binder and admixture systems for high-performance concrete.

2.2. Scope of investigation

As summarized in Table 1, the testing program involved the evaluation of mortar mixtures prepared with four different mixture compositions. Rheological parameters, variations in electrical conductivity and heat flux were determined to monitor the kinetics of formation of hydration products during the dormant period for mixtures made with various types of HRWRA (PNS and PCP) and at temperatures varying between 10 and 30 °C. Both the yield value and plastic viscosity were monitored; however, only the results of the variations of the former rheological parameter with time and temperature are presented in this paper. The results of the plastic viscosity will be highlighted in a future publication.

Table 1
Summary of experimental program

Mortar	M1	M2	M3	M4
Calorimetry	Isothermic	Isothermic	Isothermic	Semi-adiabatic
10 or 12 °C	X	X		X
15 or 18 °C	X	X	X	X
20 or 23 °C	X	X	X	X
25 or 27 °C	X	X		
30 or 32 °C		X	X	X
Conductimetry		X		X
Temperature rise	X	X	X	X
Rheology with coaxial rheometer	X	X	X	X

X refers to tested combinations.

The four mortar mixtures (M1 to M4 mortars) are based on SCC mixtures whereby aggregate particles greater than 315 μm are excluded from the mixture. The first mortar (mixture M1) was based on SCC used for the extension of hospital building in Northern France. During the construction, the concrete was cast at ambient temperatures varying between 5 and 30 °C, depending on the season; however, no special provisions to adjust the mixture composition and water demand to the temperature of the fresh concrete was made. In some cases, concrete was cast 90 min after the end of mixing, yet it was still required to exhibit sufficient self-consolidating characteristics to permit casting without mixture adjustment on site. Consequently, the SCC was proportioned with a relatively high water-to-binder ratio (W/B) of 0.53, given that the specified 28-day compressive strength was limited to 32 MPa. This non-air entrained concrete was proportioned in compliance with French NF P 18305 and European EN 206 standards for use as a ready-mix concrete in a non-aggressive environment.

The proportioning of mixtures M2 and M3 was done as a variant of the SCC used for the hospital construction. In the case of the M2 mixture, a PCP-based HRWRA was incorporated instead of the PNS–HRWRA used in the M1 system. The fluidity of both the M1 and M2 mixtures was kept constant in order to highlight the effect of HRWRA type on superplasticizer demand. In the case of the M3 mixture, Class F fly ash was used as a replacement of part of the cement volume, without altering the W/B, and hence, the paste volume fraction. The testing procedures used to assess the rheology and calorimetry of the M1, M2, and M3 mortars were identical. On the other hand, unlike the isothermic calorimetry that was conducted in the case of the M1 to M3 mixtures, semi-adiabatic calorimetry was used to monitor the kinetics of cement hydration in the case of the M4 mortar since an isothermal calorimeter was not available at the time.

Since the M1 to M3 mortars were made with the same cement, the M4 mixture was prepared using a ternary cement to ensure that results are not dependent on the cement characteristics. The M4 mortar was proportioned with 0.42 W/B and is based on SCC used in repair operations in Canada. The reference concrete mixture incorporates ternary cement made with silica fume and fly ash. Typically, such concrete is air-entrained and is made with VEA to enhance stability. However, for the sake of this investigation on mortar systems, no VEA was incorporated and the mortar was not air-entrained to enable the comparison with M1 to M3 mixtures.

3. Experiments

3.1. Materials and mixture proportioning

This study was undertaken on mortar mixtures extracted from original SCC mixture designs taking into account the binder, liquid phase (water and admixtures), and fraction of sand retained on the 315 μm sieve. The cut-off of sand fraction at 315 μm for mortar was chosen to enable the assessment of rheological properties of the system without the risk of blockage or slippage inside the bowl [13], using a coaxial rheometer for which the difference between the inner and the outer radius was only of 1 mm. Table 2 summarizes the mixture proportioning for the tested mortars, and Table 3 presents the physical and chemical properties of the selected binders.

The dosage rates of the HRWRA were determined in order to obtain the same flow time using a modified Marsh cone of the M1 to M3 mortars [14]. The targeted time was 78 s for a Marsh cone opening of 8 mm of a capacity of 1200 mL to achieve a flow of 1000 mL of the mortar. In the case of the M4 mortars made with ternary cement, the HRWRA dosage was again adjusted to attain the targeted flow time of 78 s.

CEM II B 32.5 R complying with the French NF P 15-301 standard was used for the M1 mortar. This cement contains approximately 21% of granulated blast furnace slag and 6% limestone filler. Crushed limestone sand with a fineness modulus of 2.60, limestone filler, and PNS–HRWRA incorporated at 0.28% of cement mass were used in preparing the M1 mixture. The M2 mixture was prepared with the same materials and mixture proportioning as that of the M1 mixture, except for the use of PCP–HRWRA. The SCC from which the mortars were extracted for the M1, M2, and M3 mixtures had approximately the same slump flow of 600 mm. The demand of the polycarboxylate-based HRWRA in the M2 mixture was 0.267%, which is similar to those obtained with the M1 and M3 mixtures made with PCP- and PNS-based HRWRA. This similarity in superplasticizer demand is due to the relatively high W/B of 0.53 of the reference SCC mixtures.

Table 2
Mortars mixture proportioning tested at various temperatures

Materials	Mortar			
	M1	M2	M3	M4
CEM II B 32.5 cement (kg/m^3)	837	837	732	–
Type 10 cement (for 10E SF-FA ternary) (kg/m^3)	–	–	–	705
Silica fumes (kg/m^3)	–	–	–	58.7
Fly ash (kg/m^3)	–	–	76.3	215.5
Sieved sand ($\leq$315 μm) (kg/m^3)	728	728	728	686
Polycarboxylate–HRWRA (% of cement mass)	–	0.267	0.267	0.4
Polynaphtalene–HRWRA (% of cement mass)	0.28	–	–	–
W/B	0.53	0.53	0.53	0.42

Table 3
Characteristics of two cements used in this investigation

	Chemical composition		Physical characteristics	
	CEM II B cement	10E SF-FA Ternary cement	CEM II B cement	10E SF-FA Ternary cement
SiO_2	22.4	29.3	Blaine fineness: 320 m^2/kg	Blaine fineness: 460 m^2/kg
Al_2O_3	6.2	8.6	Specific gravity: 3.05	Specific gravity: 2.93
Fe_2O_3	2.7	6.0		
CaO	58.8	46.8	Setting time (Vicat)	Setting time (Vicat)
MgO	2.2	1.75	•Initial: 180 min	•Initial: 185 min
NaO_2 Eq.	0.73	0.62		•Final: 280 min
			Compressive strength	Compressive strength
C_3A	9.0	2.6	•2 days: 21 MPa	•3 days: 20 MPa
			•28 days: 48 MPa	•7 days: 26 MPa

As mentioned earlier, the M3 mortar is based on a slightly different SCC mixture than that used for mixtures 1 and 2. In the M3 mortar, Class F fly ash was used as replacement of 12.5% of the cement volume, without altering the paste volume. This choice was made to keep the paste-to-aggregate volume ratio constant, thus enabling comparison between the two SCC in terms of rheology. Otherwise, the M3 mixture had the same mixture proportioning and materials as that of the M2 mortar.

In the case of the M4 mixture, the SCC from which the mortar was extracted had a slump flow of 650 mm. A ternary binder (CSA A510-SF/FA), containing 72% Type 10 Portland cement complying with CSA-CAN A5, 5% silica fume and 25% fly ash replacements, by mass of binder, was employed. Natural siliceous sand with a fineness modulus of 2.35 was employed. A PCP–HRWRA was used at a dosage of 0.4%, by active mass of binder.

3.2. Test methods

The mortar mixtures were prepared in batches of 6 liters in a mixer with paddles rotating helicoidally at successive speeds ranging between 140 and 285 rpm. The temperature of the raw materials was adjusted to the targeted temperature of the fresh mixtures indicated in Table 1. In order to avoid heat loss or gain during mixing, the mixer, mixing bowl, and pan of the coaxial rheometer were also maintained at the targeted temperatures. The mixing procedure consisted of adding the water and HRWRA into the mixer, then introducing the binder gradually over 30 s with the mixer turning at 140 rpm, as recommended in ASTM C 105. The sand was gradually introduced over 30 s while the mixer was still turned on. The mortar was then mixed during 30 s at 285 rpm. After a rest period of 90 s, the mixing was resumed for an additional 60 s at 285 rpm.

At the end of mixing, samples were taken to monitor heat generation during the dormant period of cement hydration. Rheological measurements were determined at predetermined intervals. In order to avoid evaporation, the mortar was kept in the mixing bowl, covered with a plastic sheet at isothermal temperatures matching the targeted test temperatures. In order to ensure homogeneity before the evaluation of rheological parameters, the mortar was remixed at a low speed of 140 rpm during 60 s.

A 350-mL sample was used for the rheological measurement using a coaxial cylinder viscometer. The surfaces of the inner and outer cylinder of the viscometer were not roughened since the materials tested in this investigation were highly flowable. The apparent viscosity was determined, after a stabilization time of 20 s, at five rotation speeds varying between 3 and 300 rpm, which correspond to shear rates of 5.1 to 510 s^{-1}. Apparent viscosity (μ_{app}) is measured as the ratio between the shear stress (τ) and shear rate ($\gamma^{\bullet}$) at a given shear rate. Yield value (τ_0) refers to the resistance of the material to undergo initial flow, and the plastic viscosity (μ) refers to the slope of the shear stress–shear rate relationship. As the up and down curves coincided, the τ and μ values were derived by regression analysis using the shear stress–shear rate data, assuming a polynomial response. The second-order value is considered as insignificant and is suppressed. The resulting expression can be expressed as $\tau=\tau_0+\mu_p\gamma^{\bullet}$ representing the behavior of a Bingham fluid. Repeatability experiments carried at 15 and 20 °C for the M1 to M3 mixtures and at 18 and 23 °C for the M4 micro mortars showed little dispersion of the results. The maximal relative deviation was of 6% for both yield value and plastic viscosity for the mixtures tested on data presented herein. After each rheological test, the sample was thrown in order to ensure confidence in test results.

For M1, M2, and M3 mortars, isothermic calorimetry was adopted [15]. The reference SCC mixture, from which these mortars are extracted, was used in the construction of wall elements 160 mm in thickness. The use of isothermic calorimetry, whereby the temperature of the test sample is maintained at the targeted temperature, can correspond to actual conditions in which concrete is cast in relatively narrow sections where the temperature is highly affected by ambient temperature. The use of isothermic calorimetry is then more appropriate than that of semi-adiabatic calorimetry to assess heat flux in relatively thin sections. For isothermic calorimetry measurements, the targeted temperature of an isolated prismatic sample measuring 90 × 90 × 160 mm^3 was maintained through the testing period, and the heat flux (Φ) required by the apparatus to cool down the sample during cement hydration is monitored using special flow cells. The temperature of the water system used to cool down the cementitious sample is controlled by six thermocouples on each side of the formwork and one maintained in the middle of the prismatic sample. A maximal variation of temperature between the core and the surface of the sample of 0.5 °C is obtained for a test temperature of 30 °C. Since the heat flux is measured on each surface of the prismatic sample (S_i, m^2), the variation of the heat of hydration, $Q(t)$, is obtained by integrating the heat flux (Φ, W/m^2) data over time. The $Q(t)$ function is normalized by the cement mass (m_c) used in fabricating the test sample, as follows (Eq. (4)):

$$Q(t) = \frac{1}{m_c}\sum_{\text{surfaces}}\int_0^t \Phi(t)\mathrm{d}tS_i. \tag{4}$$

For the M4 mortar, a semi-adiabatic calorimetric method was adopted [16,17]. However, semi-adiabatic calorimetry results and heat curves can be correlated to the isothermic results [15]. In the semi-adiabatic calorimetric method, a cylindrical sample measuring 150 mm in diameter and 300 mm in height is introduced into an isolated cell of a given heat loss coefficient (α). The increase in temperature due to cement hydration, $\theta(t)$, is then measured. The heat of hydration (Q), expressed in joules per gram of binder (J/g), is obtained by adding the heat produced by the binder and the integration of the lost heat flux over time. This value is normalized by the cement mass in the test sample. The thermal capacities (c_i) of all raw materials used in proportioning the mortar and heat loss coefficient are also used in calculating the normalized heat of hydration function, as follows:

$$Q(t) = \frac{1}{m_c}\left(\sum_i m_i c_i \theta(t) + \int_0^t \alpha\theta(t)\mathrm{d}t\right) \tag{5}$$

where m_i is the mass of each component of the mixture (g), m_c is the mass of the cement (g), c_i the thermal capacity of each component of the mixture (J/g/s), and $\theta(t)$ is the history of the temperature inside the sample, taking the room temperature as reference.

The monitoring of rheological parameters was terminated when an increase of heat flux ϕ (W/m^2) was obtained from the calorimetric testing, as illustrated in Fig. 1. Instead of considering the end of the dormant period of cement hydration to correspond to the intersection of the slope of the heat of hydration (Q) during the dormant period and the slope of Q during the accelerated period of cement hydration, the end of the dormant period is defined from the heat flux (ϕ) curve, as defined in Fig. 1 with the t_f parameter. The t_f value corresponds to the first loss of linearity of the ϕ vs. time chart. This reflects the beginning of the accelerating period where an evolutive flux due to acceleration of the rate of cement hydration takes place, resulting in an increase of heat flow [15,18]. The t_f value is established when an increase in heat flow superior to the standard variation calculated on data collected digitally during the steady period of heat flow is observed.

Changes in electrical conductivity were monitored for the M2 and M4 mortar using a twin galvanized plate separated by 5 mm of a non-conductive material. An electrical current was sent into the cell and the electrical potential difference was measured to calculate the resistivity of the mortar between the twin plates. To avoid electrolyze of the solution between plates, the electrical current was sent by impulses. Prior to each test, the cell was calibrated with a reference solution of salt and distilled water. Consequently, knowing the reference conductivity of the solution for the test temperature (T) and monitoring the effective conductivity, the cell constant, which is a function of the targeted temperature, $k(T)$, can be calculated using Eq. (6):

$$k(T) = \frac{\text{solution reference conductivity } (T)}{\text{effective conductivity}}. \tag{6}$$

Absolute conductivity is thus calculated by multiplying the monitored resistivity with the cell constant. The evolution of the electrical conductivity, given in mS/cm, indicates ionic concentration changes within the mortars. It explains the

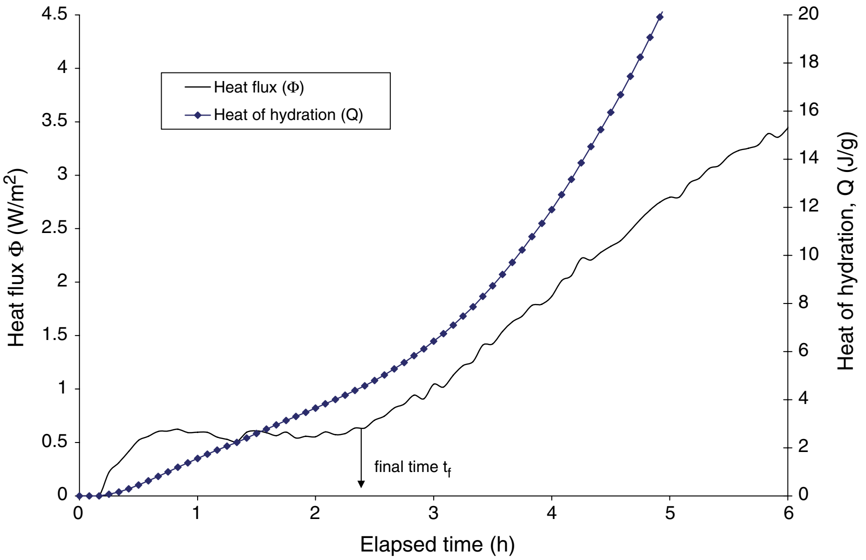

Fig. 1. Variations of heat of hydration (Q) and heat flux (Φ) with time for the M1 micro mortar tested at 27 °C using isothermic calorimetry.

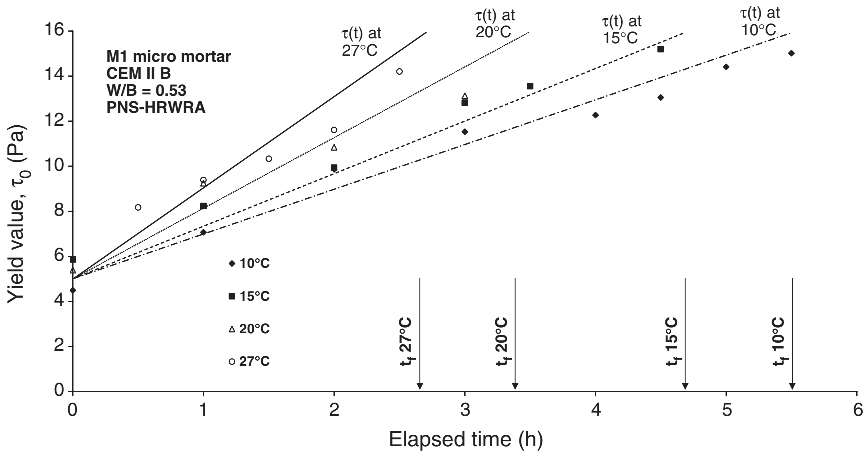

Fig. 2. Evolution of yield value with time for the M1 micro mortar tested at various temperatures: experimental data and linear models are shown.

variations in rheology through hydrates formation, which involves changes in electrical conductivity of the material.

4. Results and discussion

4.1. Coupled effect of temperature and time on changes in yield value of mortars made with PNS–HRWRA

In order to compare the variations of τ_0 with time of mixtures prepared at various temperatures, a non-dimensional parameter (t') is used. This normalized t' value can vary between 0 and 1 and is defined as the elapsed time after the contact of cement with water divided by the time corresponding to the end of the dormant period ($t'=t/t_f$). Thus, the use of the t' value enables the comparison of the variation in rheology of various mixtures cast at different temperatures at the same relative time scale [9].

As shown in Fig. 2, the τ_0 values of the M1 mortar prepared with PNS–HRWRA at various temperatures (10 to 27 °C) vary in a linear fashion with time; these variations can be fitted in linear regressions with R^2 values greater than 0.90. The rate of increase of τ_0 with time is shown to increase with temperature, although initially there is no significant difference between the τ_0 of mixtures prepared with different temperatures. This can be due to the relatively high W/B of 0.53 used in the M1 mixture. The same data presented in Fig. 2 is illustrated in Fig. 3 where the variations in yield value of mixtures prepared with different temperatures is expressed in terms of the normalized t' value. This can enable the elimination of the effect of temperature and other mixture parameters affecting the duration of the dormant period. As shown on Fig. 3, the yield value varies in a linear way with the normalized time t'. Moreover, this variation is independent of temperature.

Petit et al. [9] showed that the evolution of yield value of mortar made with PNS-based HRWRA is dependent mainly on mixture temperature. Temperature acts here as a “catalyst” that accelerates or slows down the hydration of cement. Thus, comparing the evolution of rheological parameters using the same scale of relative time shows a unique variation for all tested mixtures, independently of material temperature. Regardless of the temperature and adsorption of the HRWRA initially for the M1 mortar, the rate of formation of hydrates, which is related to the slope of the variation of τ_0 with t', is constant (Fig. 3).

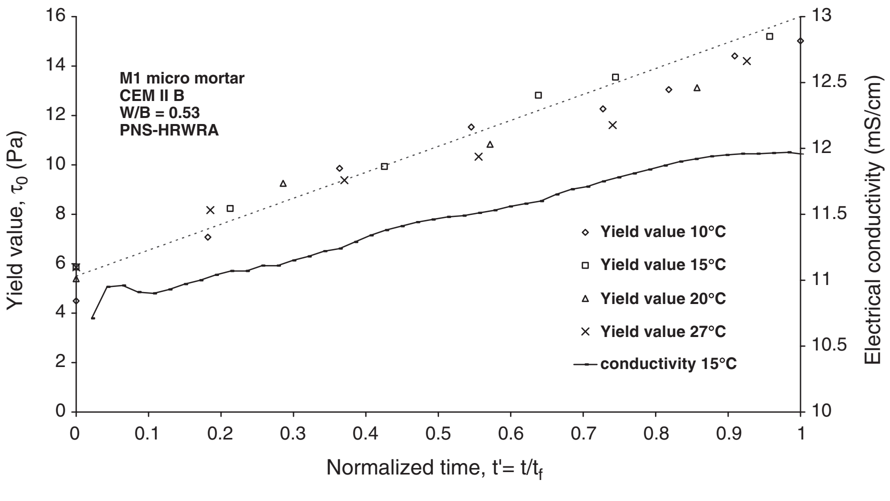

Fig. 3. Variations in yield value and electrical conductivity with normalized time of the M1 mixture tested at various temperatures.

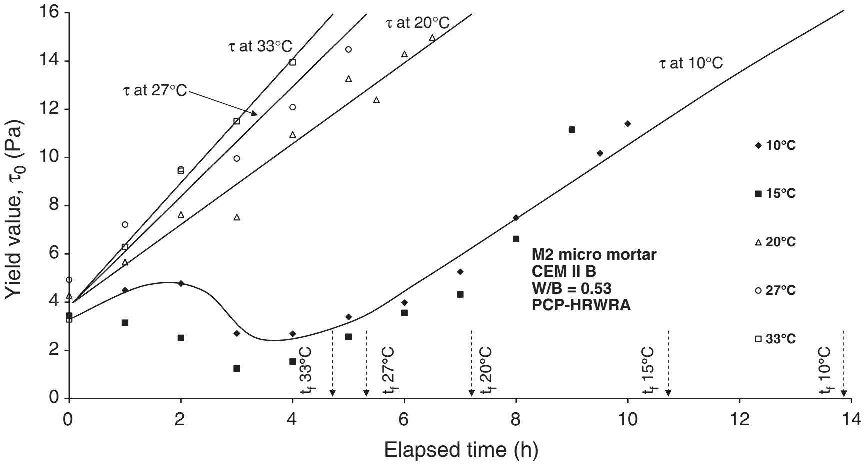

Fig. 4. Evolution of yield value with time for the M2 micro mortar tested at various temperatures.

4.2. Coupled effect of temperature and time on changes in yield value of mortars made with PCP–HRWRA

As shown in Fig. 4, the yield value of the M2 mortar varies in a linear way with time for mixture made with 20, 27, and 33 °C. This was not the case for mixtures prepared at 10 and 15 °C where the yield value exhibited some decrease initially before increasing after approximately 3 to 4 h. The M2 mortar was proportioned with 0.53 W/B and PCP–HRWRA.

Variations in yield value with the normalized t' value of the M1 and M2 mixtures prepared at different temperatures are compared in Fig. 5. The data clearly indicate the presence of a critical temperature between 15 and 20 °C for the M2 mixture where variations of τ_0 with time change from linear increase to initial reduction with time, followed by a sharp increase in τ_0. When the mixture temperature exceeds this threshold value, τ_0 is shown to vary linearly with either the elapsed time (Fig. 4) or the normalized time (Fig. 5) for both the M1 and M2 mixtures prepared with PNS– and PCP–HRWRA, respectively. Similar results were obtained with the M3 and M4 mortars prepared with the PCP–PNS–HRWRA. The threshold temperature for the M3 mixtures tested at 18 to 33 °C is not attained, and all mixtures undergo an initial decrease in yield value before undergoing subsequent gain in τ_0 (Fig. 6).

For mixtures prepared below the critical temperature, the variation of the yield value can be separated into three stages. As observed in Fig. 4, or in Figs. 5–7 when the elapsed time is normalized to obtain the relative t' parameter, at the first hour, the yield value is shown to slowly increase or remains constant before undergoing a decrease with time. After reaching a minimum value, defined here as the "end of steric effect", an increase in the yield value will then take place up to the end of the dormant period.

The efficiency of PCP–HRWRA on dispersing cement particles is shown here to depend on the mixture temperature. Such temperature can have marked effect on the rate of adsorption of PCP–HRWRA onto cement grains, which is in turn affected by the rate of cement hydration and the concentration of sulfate ions in the aqueous solution. Yamada et al. [5] suggested that the efficiency of dispersion of cement particles is related to the concentration of sulfate ions in the cement paste solution. The adsorption of PCP–HRWRA decreases when the sulfate ion concentration is high in the aqueous phase, thus affecting the degree of

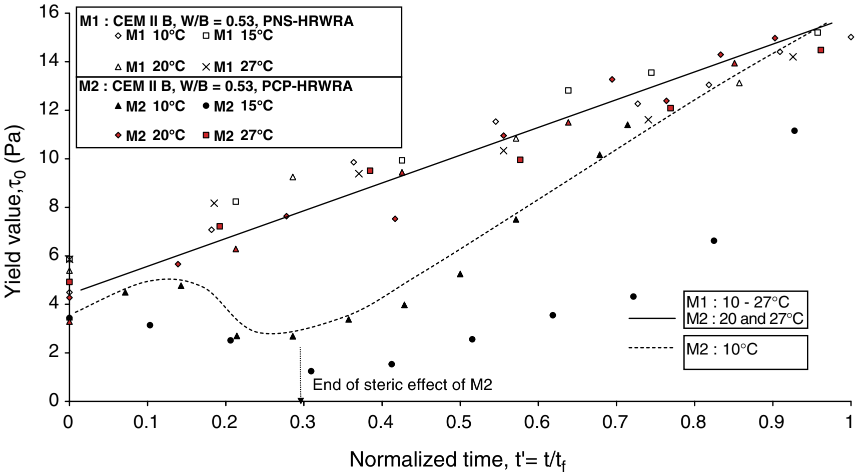

Fig. 5. Evolution of yield value with normalized time for the M1 and M2 micro mortars tested at various temperatures.

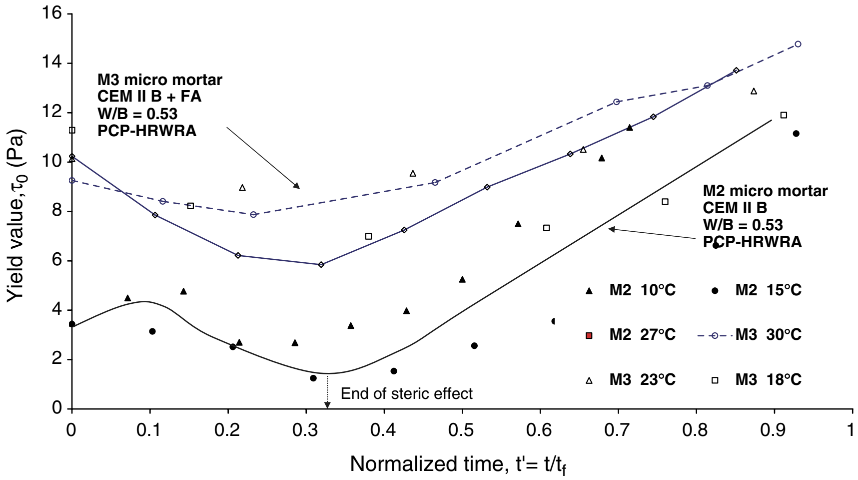

Fig. 6. Evolution of yield value with normalized time for the M2 and M3 micro mortars tested at various temperatures.

retention in fluidity with time. Yamada et al. [19] noted that a high sulfate ion concentration in the aqueous phase of cement paste at 20 °C can initially prevent the adsorption of the PCP polymer onto cement grains for mixtures proportioned with 0.3 W/B and 1% PCP–HRWRA, by mass of cement. After a given period of time, the sulfate ion concentration decreases, allowing more adsorption of PCP–HRWRA onto cement particles. During the first 30 min following the contact of cement with water, the PCP–HRWRWA adsorption was shown to increase with the decrease in sulfate ion concentration in cement paste tested at 5 °C. After 30 min, a decrease in polymer adsorption was measured in spite of the continuous decrease in sulfate ion concentration. At the lower temperature of 5 °C, a smaller increase in cement hydration and a larger decrease in sulfate ion concentration can lead to an increase in the adsorption of

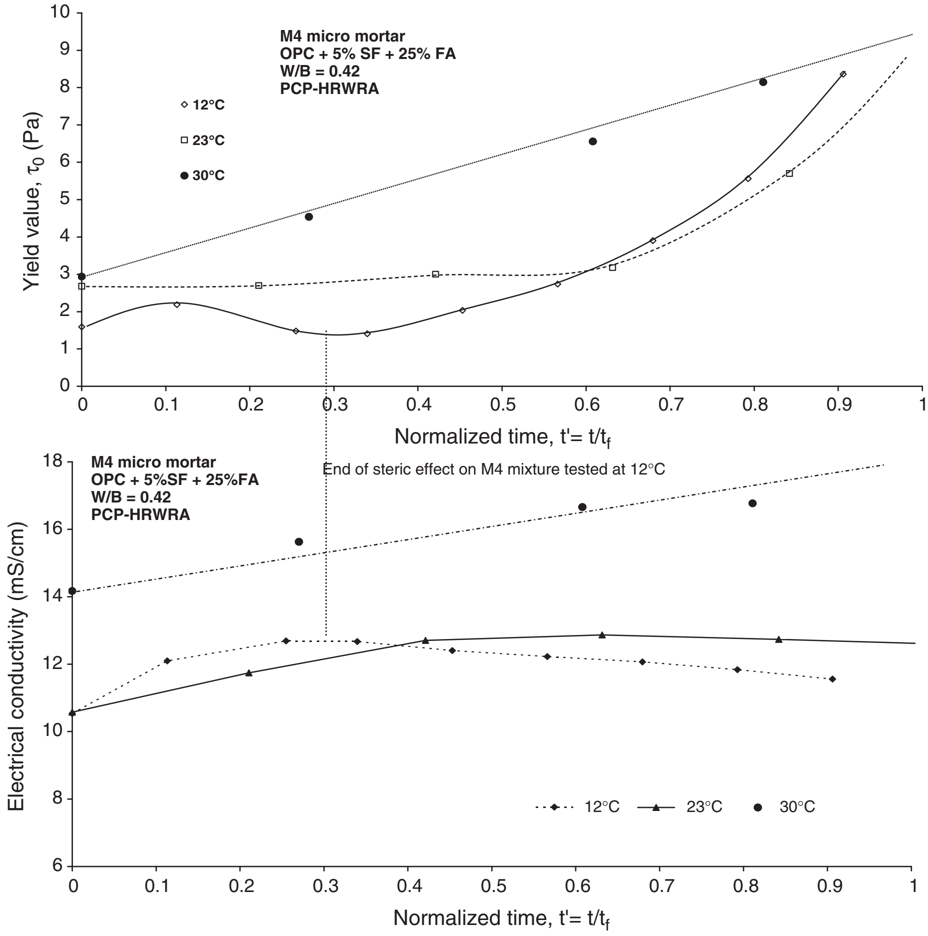

Fig. 7. Variations in yield value and electrical conductivity with normalized time of the M4 mixture tested at various temperatures.

PCP onto cement grains, thus resulting in gain in fluidity. At higher temperature, the greater increase in hydration and smaller decrease in sulfate ion concentration in the solution can decrease the degree of PCP adsorption, thus causing fluidity loss [19].

Therefore, depending on the mixture temperature, there seems to be a competition between the adsorption of the PCP–HRWRA onto cement particles and the concentration of sulfate ions in the solution. The former can promote dispersion of cement particles and enhance fluidity retention, while the latter can contribute to the shrinking of the steric size of the polymer [5], resulting in an exponential increase of the yield value. As shown in Fig. 4, the former phenomenon is observed for the mixtures made at 10 and 15 °C that lie below the critical temperature. With the progress of cement hydration of the M2 mixture at 10 and 15 °C, increase in sulfate ion concentration at approximate t' value of 0.30 can lead to the reduction in steric size of the PCP polymer, and hence the retention of fluidity of the mixture. Beyond the so-called "end of steric effect", yield value is shown to increase until the end of the dormant period. The "end of steric effect" of the M2, M3, and M4 mixtures prepared at 10 to 15 °C corresponds approximately to a t' value of 0.3.

4.3. Coupled effect of time and temperature on variations of electrical conductivity and yield value

Both yield value and electrical conductivity of the M1 mortars made with PNS–HRWRA are shown in Fig. 3 to increase in a linear way with the normalized time (t'). The increase in conductivity of the M1 mortar prepared at 15 °C with time shown in Fig. 3 is typical of values obtained at the other test temperatures of 10, 20, and 27 °C. As mentioned earlier, the yield value of the M1 mortar proportioned with PNS–HRWRA and 0.53 W/B varies in a linear fashion with normalized time, independently of test temperature. The increase in electrical conductivity is associated with the increase of the ionic charge in the interstitial solution during cement hydration. Consequently, hydrates are formed at a constant rate (quite linear increase of conductivity), resulting in a linear variation of τ_0 with normalized time.

As was the case with yield value, changes in conductivity of the mortar made with PCP–HRWRA depend on a critical temperature above which cement hydration is accelerated, resulting in increase in both conductivity and yield value. This is illustrated in Figs. 7 and 8 for the M4 and M2 mixtures, respectively, made with PCP–HRWRA, where the variation in electrical conductivity with t' is dependent on the mixture temperature.

In Fig. 8, the change in conductivity is compared to the increase in yield value of the M2 mortar cast at 10 and 27 °C; these temperatures lie below and above the critical temperature, respectively. Mortar prepared at 15 °C exhibited similar variations in conductivity and yield value as that of the mixture tested at 10 °C. At test temperatures above the threshold limit, for example at 30 °C for the M4 mortar and 25 °C for the M2 mixture, both the conductivity and yield value are shown to increase with the t' time, as was the case for the M1 mixture made with PNS–HRWRA tested at 10 to 27 °C. On the contrary, for mortars tested below the threshold temperature, for example the M4 mixture prepared at 12 °C, changes in electrical conductivity are attenuated, despite an increase in yield value beyond the so-called "end of steric effect". Beyond t' values of approximately 0.3, rapid precipitation of hydration products could take place, hence reducing the rate of gain in conductivity that should otherwise increase towards the end of the dormant period. Further research is needed to better understand the physico-chemical phenomena that take place after the so-called "end of steric effect" in mixtures made with PCP–HRWRA at relatively low temperature, as well as the effect of shear history and test protocol on the variations in yield value with time.

5. Conclusions

The influence of the coupled effect of temperature and time on the variations in yield value of mortar mixtures derived from SCC made with various types of HRWRA was investigated.

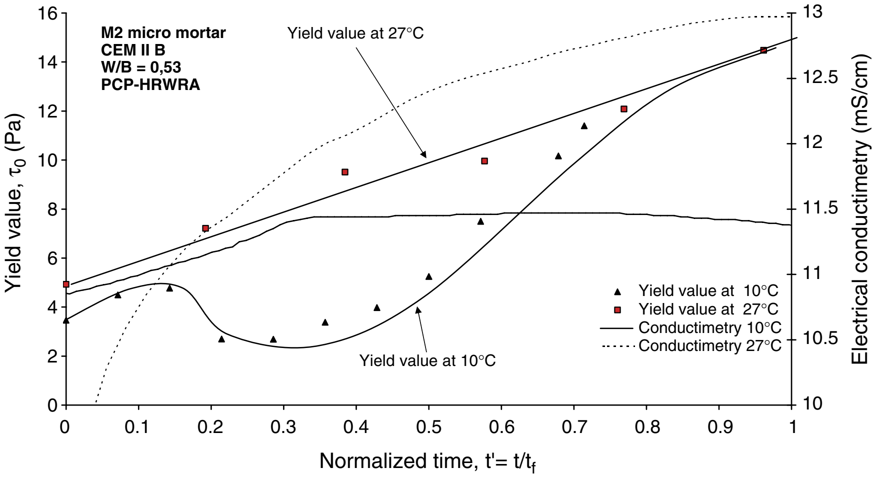

Fig. 8. Variations in yield value and electrical conductivity with normalized time of the M2 mixture tested at 10 and 27 °C.

Based on the results presented in this paper, the following conclusions appear to be warranted:

1. Yield value increases in a linear fashion with time up to the end of the dormant period (t_f) in the case of the M1 mortars made with PNS–HRWRA, regardless of the test temperature (10–27 °C).
2. The coupled effect of temperature and time can be considered through the introduction of a normalized non-dimensional time parameter t'. Such parameter takes into account the effect of mixture temperature on the duration of the dormant period.
3. In the case of the three mortars prepared with PCP–HRWRA, changes in yield value with time are shown to vary in different ways depending on mixture temperature. Below a given threshold temperature, the mortar exhibits a considerable degree of retention, or even reduction, in yield value over 30% of the dormant period. A sharp increase in yield value is observed beyond 30% of the dormant period. Above this threshold temperature, the mortar made with PCP–HRWRA behaves in a similar manner as the mixtures made with PNS–HRWRA where the yield value increases linearly with elapsed time or with the normalized time period.
4. The value of the threshold temperature of mixtures made with PCP–HRWRA was not the same for the three tested mixtures: 15 to 20 °C, above 33 °C, and 23 to 30 °C for the M2, M3, and M4 mortars, respectively. These mixtures were proportioned with different binder types and with W/B of 0.53, 0.53, and 0.42, respectively.

References

[1] C. Jolicoeur, J. Sharman, N. Otis, A. Lebel, M.A. Simard, M. Page, in: V.M. Malhotra (Ed.), Proceedings, Fifth CANMET/ACI International Conference on Superplasticizers and Other Chemical Admixtures in Concrete, ACI SP 173, ACI, Rome, 1997, p. 379.

[2] E. Sakai, Y. Kazuo, A. Ohta, Adv. Concr. Technol. 1 (1) (2003) 16.

[3] S. Hanehara, K. Yamada, Cem. Concr. Res. 29 (8) (1999) 1158.

[4] P.C. Aïtcin, C. Jolicoeur, J.G. McGregor, Concr. Int. 5 (1994) 45.

[5] K. Yamada, S. Ogawa, S. Hanehara, Cem. Concr. Res. 31 (3) (2001) 375.

[6] K. Yamada, S. Ogawa, S. Hanehara, in: V.M. Malhotra (Ed.), Proceedings, 6th CANMET/ACI International Conference on Superplasticizers and Other Chemical Admixtures in Concrete, ACI SP 195, Nice, 2000, p. 367.

[7] K.H. Khayat, M. Saric-Coric, in: V.M. Malhotra (Ed.), Proceedings, 6th CANMET/ACI International Conference on Superplasticizers and Other Chemical Admixtures in Concrete, ACI SP 195, Nice, 2000, p. 249.

[8] J. Golaszewki, J. Szwabowski, Cem. Concr. Res. 34 (2) (2003) 235.

[9] J.Y. Petit, E. Wirquin, B. Duthoit, Cem. Concr. Res. 35 (2) (2005) 256.

[10] J.Y. Petit, K.H. Khayat, E. Wirquin, Methodology to evaluate the coupled influence of time and temperature on rheological properties of cement-based materials, submitted for publication to ACI material journal.

[11] Y. Yamamoto, S. Kobayashi, Am. Concr. Inst. 83 (1) (1986) 80.

[12] A.M. Alshami, A.R. Sabouni, A.H. Bushlaibi, Cem. Concr. Res. 23 (3) (1993) 562.

[13] K.H. Khayat, A. Ghezal, M. Hadriche, Mater. Struct. 33 (229) (2000) 338.

[14] ASTM C 939, Test Method for Flow of Grout for Preplaced-Aggregate Concrete (Flow Cone Method). Annual book of ASTM Standards 04.02.

[15] H. Kada, E. Wirquin, B. Duthoit, Cem. Concr. Res. 30 (2) (2000) 301.

[16] A. Kouakou, C. Legrand, E. Wirquin, Mater. Struct. 29 (191) (1996) 444, (in French).

[17] L. D'Aloia, Determination of concrete apparent activation energy: application of the equivalent time method in order to forecast compressive stress at early ages: experimental, mechanical and calorimetric approaches, numerical simulations, Ph.D. Thesis, Ecole Nationale des Travaux Publics, Lyon, 1998, 511 p. (in French).

[18] H. Uschikawa, K. Ogawa, S. Uchida, Cem. Concr. Res. 15 (4) (1985) 561.

[19] K. Yamada, T. Yanagisawa, S. Hanehara, in: A. Skarendahl, O. Petersson (Eds.), 1st International RILEM Symposium on Self-Compacting Concrete, The publishing company of RILEM, Stockholm, 1999, p. 437.