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Influence of temperature on yield value of highly flowable micromortars made with sulfonate-based superplasticizers

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Abstract

Self-consolidating concretes (SCC) were proved to be very dependant on concreting temperature and the elapsed time. To enhance the concreting conditions of these flowable concretes, it is important to have a better knowledge of their rheological behavior, depending on the kind of superplasticizer used. The variation of the plastic viscosity and the yield value with the elapsed time and temperature must be accurately quantified. However, the methods of measuring these parameters are expensive and unsuitable with a good forecast of the material behavior due to numerous parameters that interact with each other. A simplest method to study the variation of these rheological parameters, depending on the mixture design, is proposed, using the micromortar, which derivates from the studied SCC. Moreover, to forecast the concrete behavior on the site, a simple thermodynamical approach of the cementitious matrix behavior through the study of the hydration kinetics is described.

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

1. Introduction

Organic admixtures, such as water and high-range water reducers (HRWR), are incorporated in the concrete to enhance its workability. They could either increase the strength by allowing a reduction in the water amount to be used or reduce water and cement contents for a given strength and workability.

An important class of those polymers is the polynaphtalene sulfonate (PNS), which, since 1938, has been known as cement-dispersing agents [1]. The benefit of synthetic polymers, such as PNS and polymelamine sulfonate (PMS), was developed further. But problems also appeared while using them at a high dosage to get either high-performances concrete for strength and durability or self-consolidating concrete (SCC) for workability. This problem is called cement–HRWR incompatibility, due mainly to the action of sulfonate groups within the hydration reaction and cementitious ionic matrix [2].

Although it is important to study cement–HRWR compatibility with sulfate concentration, it is not the only parameter that leads to abnormal behavior, such as delay or fast setting. Temperature also affects the level of incompatibility.

The influence of ambient temperature on the setting of cement is well documented [4]. It was found that high temperature accelerates the setting of cement, regardless of the presence of set retarder. It was also found that the use of silica fumes as a partial replacement of cement decelerates, in general, the setting of the paste; the higher this replacement is, the greater the effect becomes [5].

Temperature also influences rheology through various mechanisms. For mixtures made with PNS HRWR, adsorbed and residual polymer in the aqueous phase varies given the temperature of the fresh paste [6]. Nevertheless, the coupled effect of the HRWR, temperature and the elapsed time on highly flowable micromortars and SCC is not well documented.

The main objective of this study is to investigate the influence of temperature on the yield value τ_o of highly flowable mortar mixtures made with PNS and PMS HRWR. Moreover, studies are also conducted to point out the influence of the elapsed time on τ_o, from the batching up to the end of the dormant period. Furthermore, a simple thermodynamic approach is developed to explain the changes into the interstitial solution that lead to the evolution of τ_o with time and temperature.

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To complete the investigations and explain the thermodynamic changes in the cementitious matrix, conductivity and calorimetry measurements are conducted to evaluate the kinetics of formation of hydrates during the dormant period given the coupled effect of the HRWR and temperature variations.

2. Investigations

2.1. Research significance

The potential benefit of knowing the SCC's behavior depending on the HRWR used and the concreting temperature to enhance concreting conditions is not well documented, especially for a range of time as long as the dormant period. Neither is a thermodynamical approach of what is going on into the cement grout of the SCC.

This work proposes an easier method to study SCC through their micromortars. From the data presented, a thermodynamical approach of the material's behavior is proposed, which aims at highlighting the material's behavior through the explanation of the changes in its microstructure. It aims at doing the right choice of HRWR for each site through a better knowledge of the interactions between the HRWR, the concrete, temperature and time.

2.2. Scope of investigation

Micromortar mixtures investigated in this study derivate from commercially available SCC mixtures. For example, the first SCC, from which a complete series of highly flowable mortar is extracted, was used for the extension of Bethune's Hospital in Northern France. It was important to control the rheology of the SCC with variations in temperature because the site started in wintertime, and concreting was over at the beginning of the summer. Concrete was cast between temperatures of 5 and 30 °C. Moreover, it is also important to control rheology over transportation time because it can last up to 90 min. Consequently, a control of the rheology is essential for the SCC to completely fill the formwork and spread among reinforcing bars.

To be compatible with site conditions, a range of temperature from 10 to 32 °C was either chosen or given by Hydro-Quebec. To be sure that no heat was transferred from the mixer to the samples, temperature was taken after mixing and remixing.

The experimental program consisted of two phases. A total of 11 micromortars were tested.

The first phase concerned the investigation of the effect of temperature on the variations in yield value for a micromortar made from SCC used in light structures, like beams, with a water-to-binder ratio (W/B) of 0.52 (MB series). This high ratio is due to the fact that the specified compressive strength of the original SCC mixture was only 32 MPa because the concrete was used, complying with the French standard for ready-mix concrete NF P 18 305 and the European standard EN 206, in a nonaggressive environment. Consequently, and to be as close as possible to temperature conditions inside the formwork, isothermic calorimetry, which simulates conditions in light structure with a greater effectiveness than semiadiabatic calorimetry, was chosen [7].

Table 1
Summary of experimental program

Series	MB	MC	MD
Calorimetry	Isothermic	1/2 Adiabatic	1/2 Adiabatic
10 or 12 °C	X	X	
15 or 18 °C	X	X	X
20 or 23 °C	X	X	X
25 or 27 °C	X	X	
30 or 32 °C			X
Conductimetry		X	X
Temperature	X	X	X
Rheology with coaxial viscometer	X	X	X
Total of tested mixes	4	4	3

X refers to tested combinations.

The second phase was done on a different mixture design to validate the results found in the first phase. The selected SCC had a W/B of 0.42 and was proportioned with a ternary binder containing both silica fumes and fly ashes in addition to ordinary Portland cement (OPC). No air-entraining agent (AEA) or viscosity modifying admixture (VMA) was used to be as close as possible to the first mixture and to avoid any interaction between the HRWR and VMA polymers [6]. A polynaphtalene sulfonate HRWR was used for the MC series while MD micromortars were made with a polymelamine sulfonate HRWR to compare the effect of HRWR type on the performances of the micromortars. For this phase, semiadiabatic calorimetry [8,9] was chosen, knowing that temperature and heat curves can be correlated with isothermic results [7].

The variations of electrical conductivity with time were monitored to highlight the micromortar behavior through the analysis of the rate of ionic concentration.

As summarized in Table 1, for each five temperature regimes, the following measurements were determined:

- coaxial rheological test to monitor variations in yield value with time of the micromortars,
- either semiadiabatic or isothermic calorimetry, depending on the tested series,
- electrical conductivity,
- temperature rise.

3. Experiments

3.1. Materials and mixture proportioning

This investigation was undertaken on micromortars that constitute of liquid phase and solid particles finer than 315 μ.

This choice was made to avoid blockage or nonshearing movements inside the bowl of the coaxial viscometer [10].

Micromortars are designed from the original SCC mixture, taking into account the binder, the liquid phase (water and admixtures) and the fraction of sand retained on the 315-μ sieve.

The first series (MB) is based on an SCC mixture design used in France for a hospital extension site, with a slump flow spread of 600 mm. The binder used is a CPJ-CEM II A 32.5 in accordance to the French NF P 15-301 Standard. Crushed limestone aggregates of 14-mm maximum size, limestone sand with a fineness modulus of 2.6 and limestone fillers were used. The HRWR used in the MB series is based on PNS used at a massic dosage of 0.88%, which corresponds to a dosage of dry components of 0.28%.

Series MC and MD micromortars are based on another SCC mixture design with a slump flow of 650 mm. The ternary binder used was composed of Type 20 Portland cement, complying with CSA-CAN A5, containing 6% silica fume and 22% fly ash replacement by weight of binder. The composition and characteristics of the binder used in this study are summarized in Table 2. Crushed limestone aggregates with a maximal diameter of 12 mm were used. A PNS-based HRWR was used for the MC series at a massic dosage of 0.5% by dry weight of the binder. The HRWR used for the MD series is composed of PMS incorporated at 0.8% by dry weight of binder.

The dosage rates for the micromortars were determined using the grout method [11] to get the same Marsh cone time on micromortars for the MC and MD series. The targeted time was 78 s for a Marsh cone opening of 8 mm. Table 3 gives the mixture proportioning for the SCCs and the micromortar mixture proportioning extracted from each SCC for the three tested series.

3.2. Test methods

The chosen mix design for micromortars was in compliance with ASTM C105 Standard. All micromortars were prepared in batches of 6 l and mixed in a mixer with a mixing paddle rotating from 140 to 285 rpm. The temperature of the raw materials was adjusted to be similar with those of the targeted fresh mixtures. To avoid energetic transfers during the mix, the mixer, the mixing bowl, the pan and the coaxial rheometer were also maintained at the targeted mortar temperature.

Table 2
Composition of Type 20 cement (Saint Laurent)

Chemical analysis (%)		Physical analysis
SiO_2	29.25	93% < 45 μm
Al_2O_3	8.62	Blaine surface : 460 m^2/kg
Fe_2O_3	6.03	Specific gravity 2.93
CaO	46.84	
MgO	1.75	Setting time (Vicat)
C_3A	2.63	Initial : 185 min
Equivalent NaO_2	0.62	Final : 280 min
Others	1.9	
		Compressive strength
		3 Days : 20.1 MPa
		7 Days : 25.6 MPa

Table 3
Micromortars mixture proportioning tested at various temperatures

Materials	Name	MB	MC	MD
Cement (kg/m^3)	CEM II A	837	–	–
Cement (kg/m^3)	Type 20	–	705.4	705.4
Silica fume (kg/m^3)		–	58.7	58.7
Fly ash (kg/m^3)		–	215.5	215.5
Water (kg/m^3)		439	408.6	408.6
Sieved sand (≤315 μm) (kg/m^3)		728	686	686
Naphthalene-based HRWR (% of dry weight of cement)			0.5	
Naphthalene-based HRWR (% of dry weight of cement)		0.28		
Melamine-based HRWR (% of dry weight of cement)				0.8
W/B		0.52	0.42	0.42

The mixing procedure consisted of adding water and HRWR into the mixer. The cement was then introduced gradually over 30 s, while the mixer was turned on at a rotating speed of 140 rpm. The sand was then gradually introduced during 30 s while the mixer was still on. Then, the micromortar received 30 s at a speed of 285 rpm. After a rest period of 90 s, the mixing was resumed for an additional 1 min at 285 rpm.

Prior to conducting each rheological measurement and to ensure a perfect homogeneity of the micromortar, the mixtures were mixed during 60 s at 140 rpm, even if it was demonstrated that cement grain defloculation in the suspension is thus influenced during the dormant period [12]. Even though, the resulting defloculation has no great effect because the suspension is highly flowable. As a consequence, solid particles are already dispersed into the suspension. Consequently, and even if calorimetric and electrical conductivity monitoring was done with micromortars at rest, they can be compared with rheological measurements.

A coaxial cylinder viscometer was employed to evaluate the rheological properties of the micromortars. A 350-ml sample was used for such measurement. The apparent viscosity was determined at five rotation speeds, varying between 3 and 300 rpm, which correspond to strain rates of 5.1 to 510 s^{-1}. The rheological parameters measured, using the viscometer, are shown in Fig. 1. The apparent viscosity is calculated as the ratio between the shear stress (τ)and strain rate ($\dot{\gamma}$) at a given shear rate. The yield value 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. The τ and μ values are 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 $\tau=\tau_0+\mu_p\gamma$, representing the behavior of a Bingham fluid. To avoid evaporation in

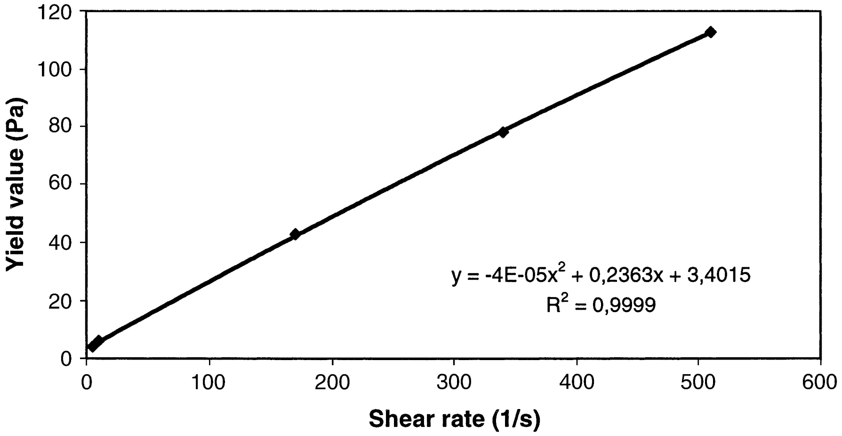


Fig. 1. Rheological parameters using a coaxial viscometer.

between tests, the mortar was kept in the mixing bowl, covered with a plastic sheet and at an isothermal temperature matching that of the targeted test temperature.

For the MB series (Table 1), the calorimetric method proposed by Kada [7] was adopted. It consists of imposing temperature to the isolated prismatic sample (9 × 9 × 16 cm) and measuring, through a series of flux sensors, the heat flux Φ given by the apparatus to cool down the heat increase in the sample due to hydratation. Because the heat flux is measured on each side S_i of the prismatic sample, the quantity of heat of hydration Q is obtained by integrating the data with time, knowing the mass of cement m_c into the sample and using the following equation (Eq. (1)):

$$Q(t) = \frac{1}{m_c}\sum\nolimits_{\text{surface}}\int_0^t \Phi(t)\mathrm{d}tSi \tag{1}$$

For the MC and MD series, the semiadiabatic calorimetric method was adopted [9]. In this method, the cylindrical sample (150 mm diameter and 300 mm height) is introduced into an isolated cell for which the heat loss coefficient α is known. The increase of temperature due to hydratation is thus 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 knowing the mixture design, all material's thermal capacity and the heat lost, which is obtained by integrating the lost heat flux with time (Eq. (2)):

$$Q(t) = \frac{1}{m_c}\left(\Sigma_i m_i c_i \theta(t) + \int_0^t \alpha\theta(t)\mathrm{d}t\right) \tag{2}$$

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

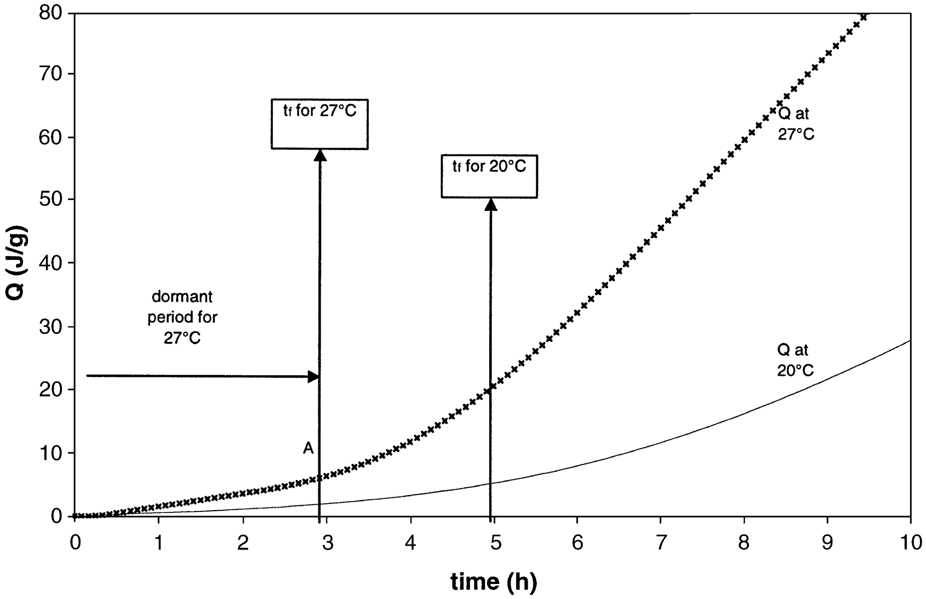


Fig. 2. Heat vs. time for mortars mixtures tested in serie MB at various temperatures with isothermic calorimetry—measure of t_f.

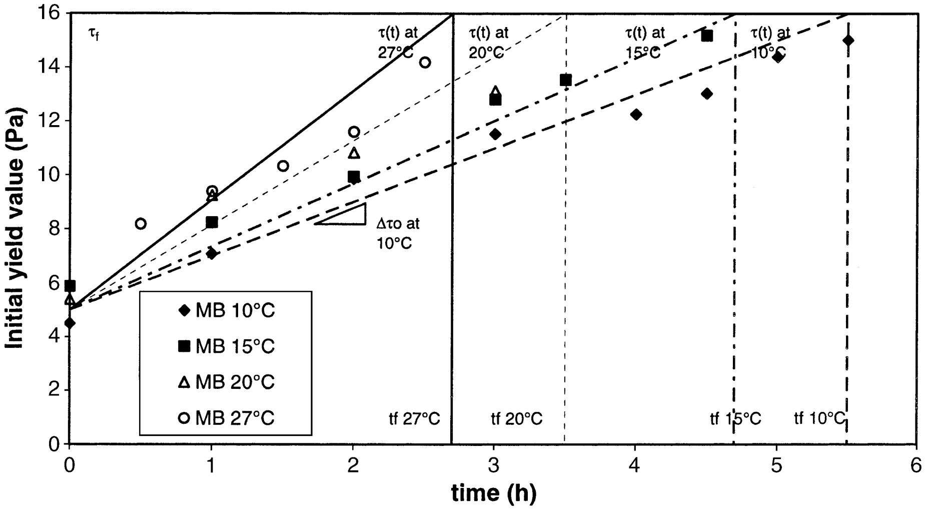


Fig. 3. Evolution of the initial yield value with time for mortars mixtures tested in serie MB at various temperatures: linear model and experimental points.

The monitoring of the rheological parameters was stopped when an increase of heat flux ϕ (W/m^2) was obtained from the calorimetric testing, as illustrated in Fig. 2, Point A. While the end of the dormant period is usually considered as the point where the tangents of the slopes of the dormant period and the heat increase due to the acceleration of hydration intersects in the heat Q with time chart [12,13], another parameter, t_f, was chosen. It corresponds to the first loss of linearity in the Q versus time relationship (Fig. 2). This parameter also corresponds to the loss of linearity in the ϕ versus time chart, which means a move from a constant to an evolutive flux. Physically, t_f corresponds to the time when the saturation rate of portlandite reaches a threshold, creating an increase of heat flux ([7,14,15]).

The electrical conductivity was monitored using a twin galvanized plate separated by 5 mm of a nonconductor material. An electrical current is sent into the cell, the electrical potential difference is then measured, and the resistivity of the micromortar between the twin plates is thus calculated. Prior to each test, the cell is calibrated with a reference solution of salt and distilled water. Consequently, knowing the resistivity of the solution and reading the effective resistivity, the cell constant k can be calculated using Eq. (3):

$$k = \frac{\text{read data}}{\text{solution resistivity}} \tag{3}$$

Absolute conductivity is thus calculated by multiplicating the read data with the cell constant. The evolution of the

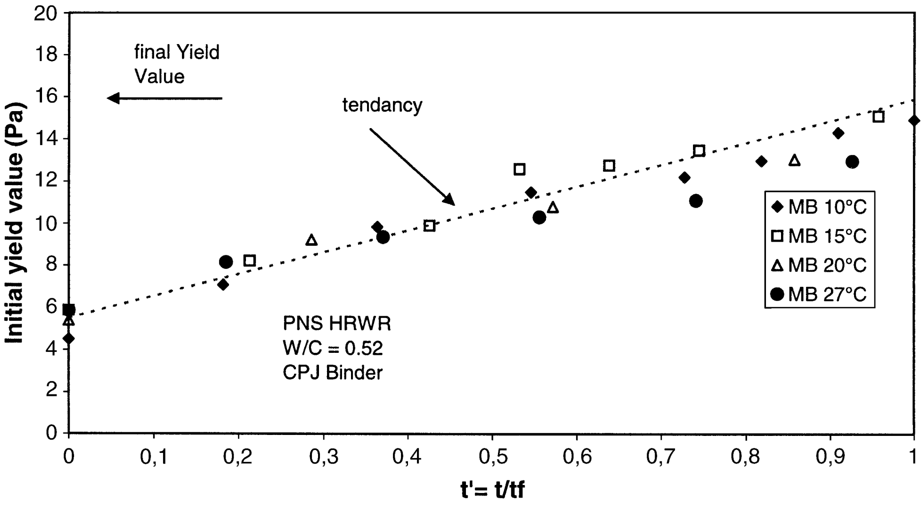


Fig. 4. Initial yield value vs. normalized time for mortars mixtures tested in serie MB at various temperatures.

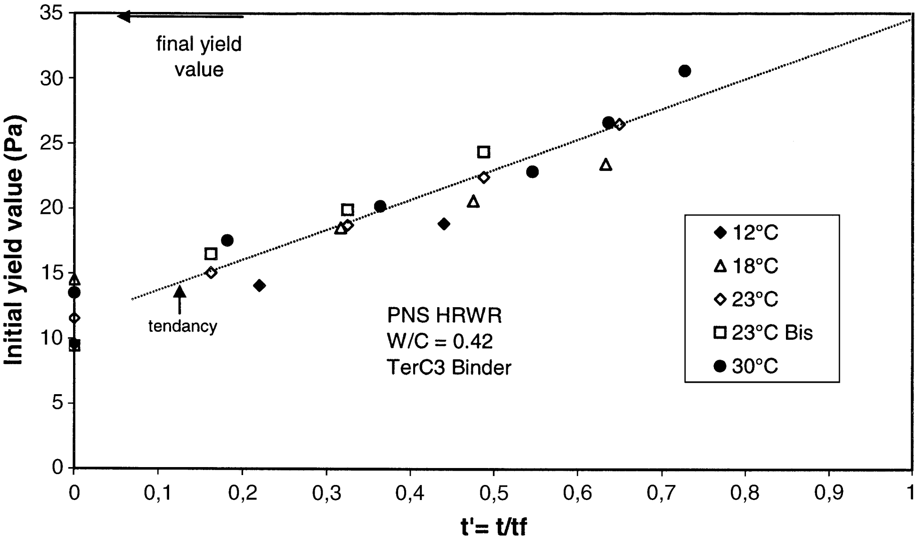


Fig. 5. Initial yield value vs. normalized time for mortars mixtures tested in serie MC at various temperatures.

electrical conductivity, given in MilliSiemens per centimeter, allows knowing the ionicity of the micromortars and, consequently, to explain the changes in rheology through hydrate formation, which changes the electrical resistivity of the material.

3.3. Tests and data processing

The chosen test methodology is:

1. batching the micromortar at the selected temperature, then filling all samples recipients for calorimetry, conductimetry and rheology,
2. in the meantime, launching the calorimetric and conductimetric tests,
3. proceeding to rheological tests every half an hour,
4. stopping rheological tests when an increase of heat flux is observed, then monitoring the time, which is taken as the final time t_f previously defined,
5. data processing using the normalized time t'.

3.4. Definition of the normalized time t'

The term t', taken as the ratio of time by final time ($t' = t/t_f$), is a dimensional parameter that allows us not to take in account secondary effects, such as delaying. It allows direct comparisons of charts at various temperatures and with different kinds of HRWR. Thus, all the parameters are studied in the same scale of time. This parameter, which varies from 0 to 1, can be compared, as it was pointed out by Laplante et al. [3], to an "equivalent age" for the dormant period because during

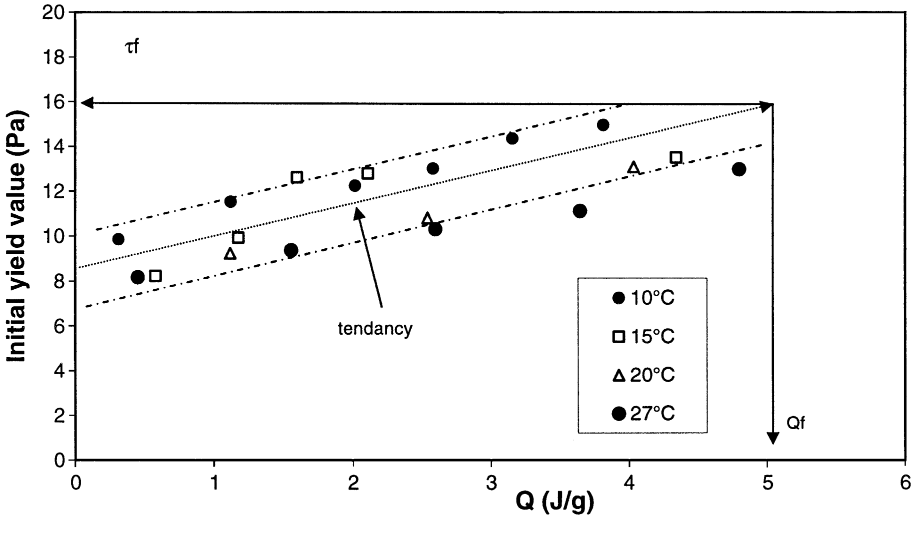


Fig. 6. Initial yield value vs. heat for mortars mixtures tested in serie MB at various temperatures.

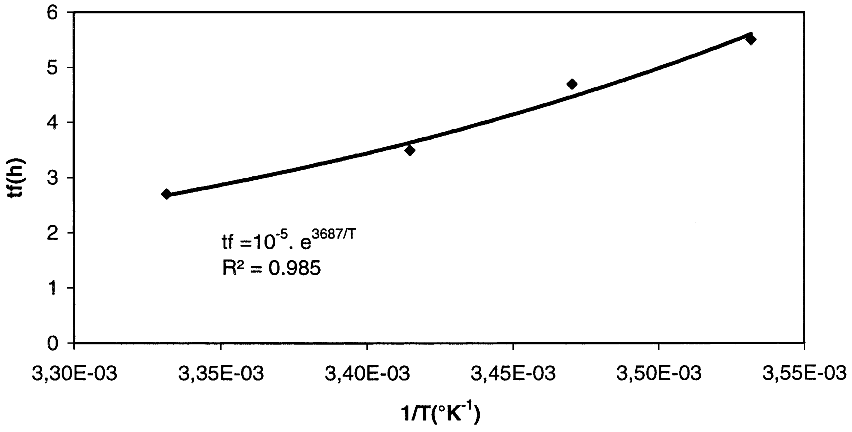


Fig. 7. Final time vs. temperature for mortars mixtures tested in serie MB.

this length of time, the hydration factor [7] α is irrelevant.

4. Results and discussion

Although τ_o and μ were monitored with time, temperature and different types of HRWR, only results concerning the yield value are presented in this paper.

4.1. Results on micromortars with PNS-based HRWR

As shown on Fig. 3, the variation of the yield value τ_o with time can be considered as linear for each test temperature. Regression coefficients between the proposed linear variation and the experimental points are all above 0.9. The slope of the lines, $\Delta\tau_o$, which is a function of the temperature T, is the increase of yield value, with time at a fixed temperature. The effect of temperature on the initial adsorption of PNS [6] is hidden by the flowability of the micromortars, although it exists. As a consequence, the initial yield value τ_o, which should be highly dependant on temperature, varies in a restricted interval of 1.5 Pa (Fig. 3).

Working with t' allows eliminating the effect of temperature and only pointing out the effect of the HRWR. The yield value varies, with normalized time t', independently of temperature (Figs. 4 and 5). A similar evolution of the yield value with Q is shown in Fig. 6. It means that, regardless of temperature, and regardless of the initial adsorption of the HRWR, the rate of formation of hydrates is constant, which translates a kinetic global reaction that leads to the same amount of formed hydrates, hence, the same final yield value τ_f and the same final quantity of delivered heat Q_f. It can be explained as follows: At “equivalent normalized time”, taking t' as a reference, the mixture passes from an initial to a final stage following a unique thermodynamic evolution that only depends on hydration kinetics. At the initial stage, Q is nil, regardless of temperature, and at the final stage, Q is equal to Q_f, regardless of temperature. More dispersion is observed on Fig. 6 compared with the previous

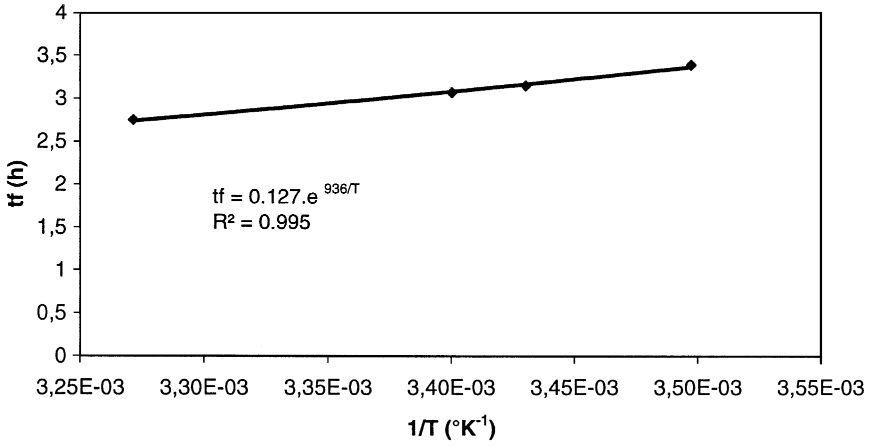


Fig. 8. Final time vs. temperature for mortars mixtures tested in serie MC.

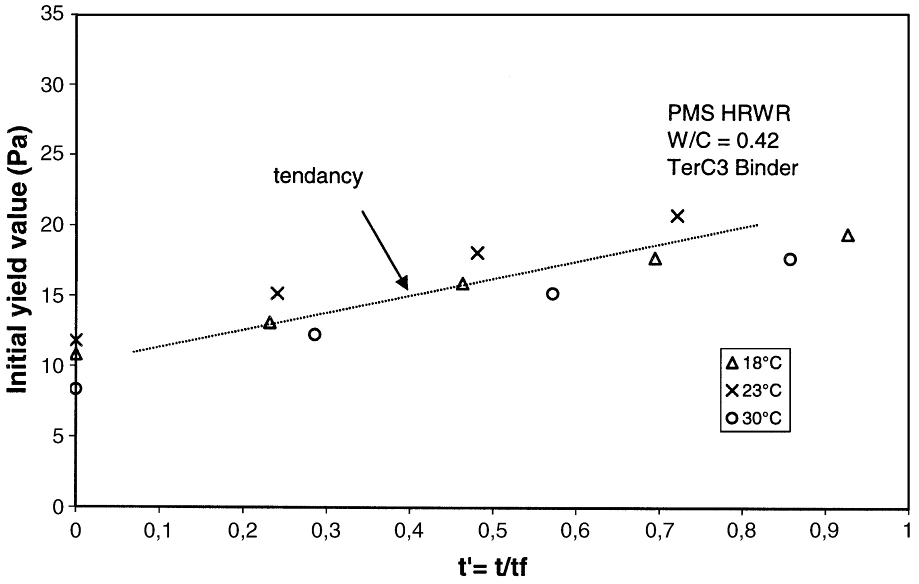


Fig. 9. Initial yield value vs. normalized time for mortars mixtures tested in serie MD at various temperatures.

ones. This is due to the measurement method: As the heat Q calculated from the measured flux or temperature is small (less than 5 J/g of binder), it affects the precision of the monitored data. Consequently, the variance between the points or the series of points is higher in that case than for the measurement of the yield value. However, the spread is around 10% on Q at various temperatures to match a unique straight evolution curve.

The parameter t_f is also given as a function of $1/T$ where T is temperature, in Kelvin (Figs. 7 and 8). An Arrhenius-like evolution is noticed and can then be written as (Eq. (4)):

$$t_f = Ae^{B/T} \tag{4}$$

4.2. Results on micromortars with PMS-based HRWR

Based on the results presented in Fig. 9, similar conclusions as those presented for series MB and MC made with PNS-based HRWR can be made for mixtures made with PMS-based HRWR (series MD). PMS acts like PNS in the solution, giving sulfate ions in addition to the one given by the initial amount of gypsum introduced into the clinker. The sulfate will react with the aluminates to form ettringite [2], thus increasing the yield value and plastic viscosity of the mixture. As it is a purely kinetic chemical reaction, temperature is only a catalyst that accelerates or slows down the reaction without changing the thermodynamics. Consequently, the mixture passes from an initial to a final stage following a unique thermodynamic evolution that only depends on hydration kinetics (initial stage: $Q=0$, regardless of temperature; final stage: $Q=Q_f$, regardless of temperature). This hydration kinetics is a global view of what is going on into the micromortar. Consequently, it includes secondary effects, such as the adsorption of water onto hydrates.

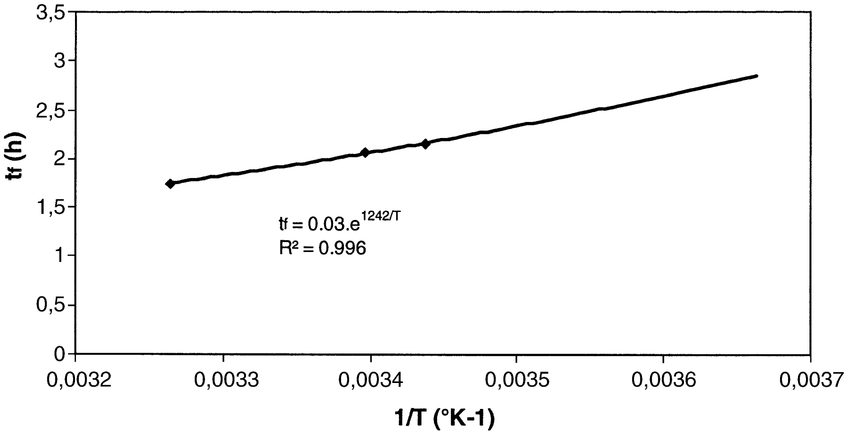


Fig. 10. Final time vs. temperature for mortars mixtures tested in serie MD.

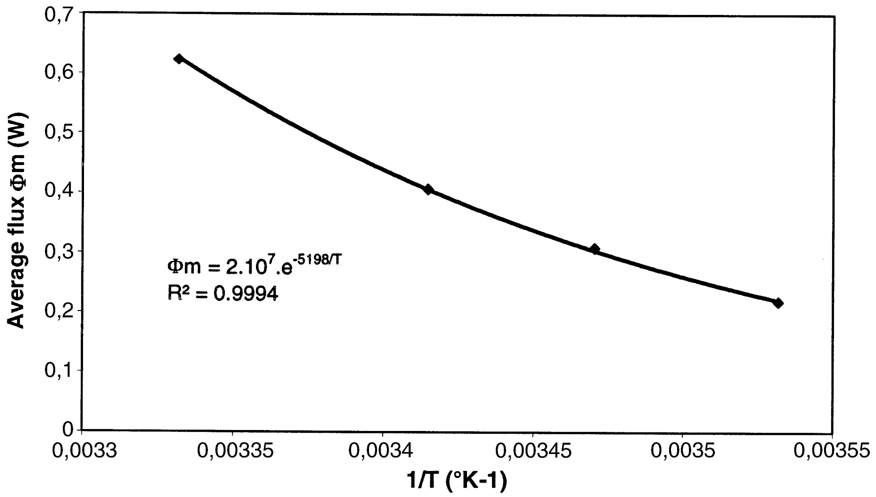


Fig. 11. Increase of the average heat flux with temperature for mortars mixtures tested in serie MB.

The evolution of the final time t_f with temperature also follows an Arrhenius-like exponential function of $1/T$ (Fig. 10).

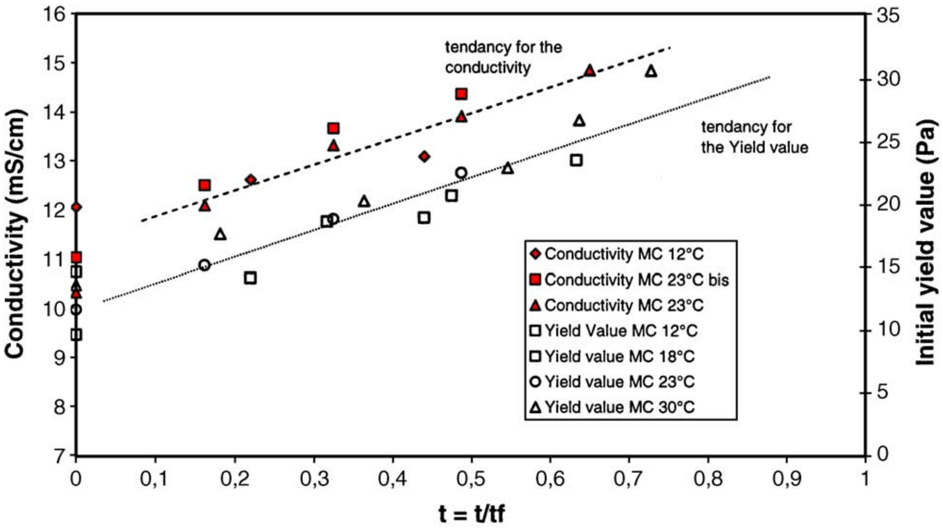
4.3. Analysis of the results using the average heat flux increase

The average heat flux Φ_m is taken as the measured heat flux (monitored or calculated by the derivation of Q with time, depending on the kind of calorimetric test used [7,9]) during the dormant period until t_f, eliminating the first points corresponding to initial precipitations [16]. During the chosen length of time, Φ_m is constant.

The exponential approach on all series in the average flux versus temperature inverse gives a good correlation, with an R^2 equals to .999 for the MB series (Fig. 11). The heat flux is following an Arrhenius-like function, which allows us to conclude that unique activation energy exists during the dormant period for each mixture, regardless of temperature, as it was observed by Laplante et al. [3]. Consequently, the hydration reaction could only be a kinetic reaction that confirms the ffsacts cited in the previous paragraph.

4.4. Analysis of the results using conductimetry

By analyzing conductivity versus t' for mixtures belonging to the MC (PNS) and MD (PMS) series (Figs. 12 and 13), it can be observed that the evolution of the conductivity with normalized time is linear, except at the very beginning of the curve. The nonlinear part corresponds to the fast reactions happening after the contact between the binder and water. Then, the evolution of the conductivity with normalized time is linear and unique, regardless of temperature. The solubility of clinker, which can be translated as the slope of the curve conductivity



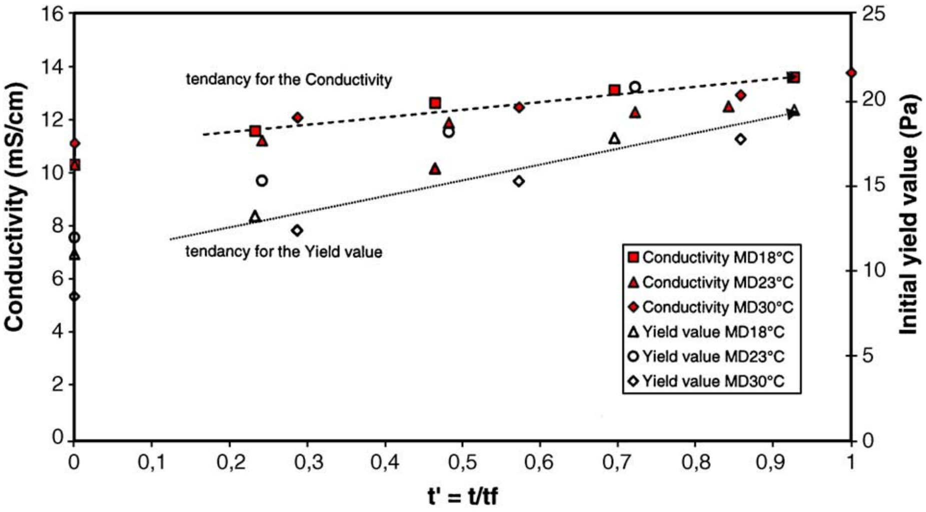


Fig. 13. Conductivity vs. t' for mortars mixtures tested in serie MD (PMS-based HRWR).

versus time, is a function of the cementary matrix and temperature: the higher the temperature is, the more the solubility of clinker increases. It is translated by an acceleration of the hydration kinetics. Similar observations had been made by Vernet [16]. This slope seems to be independent of the temperature of the mixture and lets us think that the two HRWR (PNS and PMS) act the same way by releasing sulfates into the solution and helping ettringite formation [2]. The more they deliver sulfate ions, the less they act as electrostatic repulsive force admixture by disintegration of their molecular structure. This phenomenon is due to the kinetics of hydration: When time passes, ions are released in the solution through the dissolution of binder grains and the release of sulfates in the solution by the disintegration of the HRWR polymer [2]. That explains the increase of electrical conductivity. As a consequence, there are more ''materials'' in the interstitial phase to build hydrates. Thus, it explains the unique linear evolution of the yield value for each series with time, regardless of temperature (Figs. 12 and 13).

In addition, it seems that the two used superplasticizers inhibit approximately the same amount of reactive sites on the surface of the grains because the initial conductivity of the two tested mixtures (same cementitious matrix, W/B = 0.42) are close to each other. This observation is in accordance with the ones made by Jolicoeur et al. [6]. The differences between the initial yield values are due to a difference of adsorption of the admixture on the grains depending on temperature [6].

5. Conclusions

The influence of temperature and time on the evolution of the rheological properties and heat flux of micromortars with PNS and PMS HRWR was investigated. Based on the results presented in this paper, the following conclusions appear to be warranted:

1. Regardless of the kind of HRWR, the final time is affected by temperature in an Arrhenius-like exponential evolution. This leads to the conclusion that, for each mixture, there is unique activation energy independent of temperature during the dormant period.
2. The hydration reaction of highly flowable micromortars made with PNS or PMS HRWR is purely kinetic, thermodynamically speaking. The evolution of the yield value with time is linear up to t_f.
3. The evolution of the yield value with normalized time t' or the yield value with Q is linear, from an initial to a unique final stage, regardless of the temperature.
4. The heat flux Φ shows an Arrhenius-like evolution with temperature. As a consequence, the activation energy is unique for each mixture during the dormant period, regardless of temperature. Temperature only affects the kinetics.

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