S. Al-Martini[1] *and M. Nehdi*[1]

Effect of Chemical Admixtures on Rheology of Cement Paste at High Temperature

ABSTRACT: Placement of cement-based materials in hot weather conditions encounters many problems due to the rapid evaporation of mixing water and the accelerated hydration of cement. Such materials are also adversely affected at elevated temperatures by an increased water demand, shorter setting time, and more rapid slump loss. These problems can be mitigated using adequate chemical admixtures. However, technical data on such admixtures are commonly developed at normal temperatures, and there is a real need to investigate their performance at hot temperatures. In the current research, the rheological properties of portland cement pastes with a water-cement ratio (w/c) of 0.35 and 0.50 are investigated at different temperatures in the range of 20 to 45°C using an advanced shear-stress/shear-strain controlled rheometer. The influence of water-reducing and retarding admixture, polycarboxylate, naphthalene sulfonate, and melamine-based high-range water-reducing admixtures (HRWR) in addition to mid-range water-reducing admixtures (MRWR) on the rheological properties of cement paste at various temperatures was also examined. The paper aims at formulating recommendations for the effective use of chemical admixtures at high temperature, which should enhance the rheological properties of cement-based materials in hot weather conditions.

KEYWORDS: rheology, cement paste, water-reducing admixture, high temperature

Introduction

Hot weather environments cause serious problems in the placement of fresh concrete due to the acceleration of cement hydration and faster water evaporation. Fresh concrete mixtures at high temperature tend to stiffen much faster with time compared to similar mixtures placed at moderate temperatures, and significant slump loss is usually experienced under high temperature [1,2]. This presents a real challenge in hot weather concreting because concrete does not remain workable long enough to allow time for its transporting, placement, compaction, and finishing [3].

The upper limit of ambient temperature to produce good quality concrete, as specified by ACI guidelines, is 32°C [4]. Likewise the ideal temperature of fresh concrete for its adequate placement ranges from 20–23°C [5]. Practically speaking, achieving these criteria is often not an easy task in hot weather, and various precautions are needed during concrete mixing and placement to reduce its temperature. Such precautions are usually difficult to be implemented in-situ without high additional costs.

A study conducted by Hassanain et al. [6] showed that the rate of water evaporation in hot weather is strongly related to the time of day at which concrete is being cast. For instance, the rate of evaporation in concrete cast during mornings was found to be much lower than that in concrete cast at noontime. Therefore, one of the common practices to overcome problems in hot weather concreting is to place concrete in early mornings or late afternoons when the temperature is moderate. However, this is not always a feasible solution, especially for large-scale construction projects. The economic importance of such projects and the associated strict construction schedules dictate continuous placing of concrete even at temperatures that exceed the maximum allowable limits. Generally, concrete is placed in hot weather regions, such as the Arabian Gulf, at temperatures often around 40 to 45°C [5]. To overcome the loss of concrete workability, additional mixing water is usually added to increase the fluidity of fresh concrete. However, this was found to cause significant reduction in the compressive strength of concrete and its long-term durability [4,7,8].

Using cooled water for mixing concrete is one of the common practices to reduce fresh concrete

[1] Department of Civil and Environmental Engineering, The University of Western Ontario, 1151 Richmond Street, London, ON, Canada, N6A 5B9, e-mail: mnehdi@eng.uwo.ca

temperature. However, since the amount of water used in mixing is relatively small, the effect of cooled water on reducing the temperature of fresh concrete mixtures during placing is insignificant [9]. Using ice as part of mixing water has also been a common means of reducing concrete temperature [9], and proved to be more effective than using cooled water. However, it is a costly method; and at a time when the concrete industry is striving to develop sustainable practices using energy efficient technologies and green materials, using ice in mixing concrete is against this trend.

Another method to reduce the temperature of fresh concrete in hot weather is chilling aggregates [10]. This can be done for instance by spraying liquefied carbonic acid gas at -78.5°C on fine and coarse aggregates that are mixed in a special mixer. However, no major improvement in the workability of fresh concrete has been achieved using this technique [10].

Efforts were also made to cool sand by injecting liquid nitrogen having a very low temperature (-196°C) into a sand cooling apparatus. This dropped the sand temperature to well below the freezing temperature of water, causing a drop in the temperature of the entire concrete mixture. In this technique, the fresh concrete fluidity showed slight improvement [11].

Chemical admixtures are also widely used to decrease water demand and improve concrete flowability, especially when placing concrete in highly congested reinforcement and hard-to-reach areas [12]. For instance, it was found that using a lignosulfonate-based set retarder at 0.25 % by cement mass delayed the start of heat of hydration evolution by 1 to 1 1/2 hour at a high temperature of 60°C [3].

Research was also conducted to study the effect of water-reducing and water reducing/retarding admixtures on improving concrete fluidity in hot weather at 33°C [13]. In this research, the amount of water needed to compensate for the slump loss due to high temperature was measured. Four different water-reducing admixtures were used including polyhydroxy carbonic acid (ASTM Type D), modified lignin sulfonate (ASTM Type A), modified lignin carbohydrates (ASTM Type D), in addition to one retarding admixture. It was found that using the ASTM Type D admixture was effective at delaying setting, which is important to reduce the mechanical vibration needed for compaction and the occurrence of cold joints. On the other hand, these admixtures had the adverse effect of rapid change in the consistency of fresh concrete with time [13].

Research was conducted to study the possibility of decreasing the slump loss of concrete due to temperature rise using three high-range water-reducing admixtures (HRWRAs) (naphthalene sulfonate, naphthalene sulfonate modified with a retarding agent, and naphthalene sulfonate modified with twice the dosage of the same retarding agent) [14]. It was found that in general, increasing the dosage of HRWRA decreased the slump loss at high temperature, and that the naphthalene-based HRWRA with a higher dosage of the retarding agent improved the fluidity of concrete at high temperature more efficiently than the naphthalene-based admixture alone. Also, lower dosages of the HRWR incorporating the retarding agent were needed to achieve results similar to that of the HRWR alone [14].

However, there is still a lack of information in the literature regarding the effect of various chemical admixtures, especially the new generation of superplasticizers, on the rheological properties of fresh concrete at high temperature. Typically, research and development and technical data on chemical admixtures are developed in countries with cold or moderate climates. The products and the associated technical information are then exported to countries with hot weather without adequate consideration of the local conditions. The field results in many occasions have been disappointing.

The rheological properties of cement paste play an essential role in the behavior of fresh concrete. Therefore, the rheological properties of plain cement pastes having a w/c=0.50 were investigated at temperatures of 20, 40, and 45°C. Moreover, cement pastes at a water/cement ratio (w/c)=0.35 were tested at the same temperatures (20, 40, and 45°C). These cement pastes incorporated various dosages of five different chemical admixtures, namely a glucofc-based water-reducing and retarding admixture (WRR), a polycarboxylate-based mid-range water-reducing admixture (MRWR), a polycarboxylate-based high-range water-reducing admixture (PHRWR), a naphthalene sulfonate-based high-range water-reducing admixture (SHRWR), and a melamine-based high-range water-reducing admixture (MHRWR). Experimental results allowed gaining a better understanding of the function of these admixtures at high temperature, which should lead to their effective use in the design of concrete mixtures under hot weather conditions.

TABLE 1—*Properties of ordinary portland cement used.*

Chemical Composition		Physical Characteristics	
SiO_2 (%)	19.8	Loss on ignition (%)	2.5
CaO (%)	63.2		
Al_2O_3 (%)	5.0		
Fe_2O_3 (%)	2.4	Specific surface area, Blaine	410
MgO (%)	3.3	fineness (m^2/kg)	
K_2O (%)	1.2		
SO_3 (%)	3.0		
Na_2O (%)	0.1	Specific gravity	3.17
TiO_2 (%)	0.3		
$CaCO_3$ (%)	...		

Experimental Setup

CSA Type 10 (ASTM Type I) ordinary portland cement was used in all cement pastes investigated; its chemical and physical properties are shown in Table 1. Deionized distilled water was used for mixing, and its temperature was maintained at $19 \pm 0.5 °C$. Several cement pastes were made with a water/cement ratio (w/c) of 0.50 without admixtures to verify the reliability of the testing procedure and apparatus at different temperatures. The rheological properties of cement pastes without admixtures (w/c=0.35) were also measured for temperatures of 20, 40, and 45°C. This was done to highlight the effect of the w/c on the rheology of cement paste at different temperatures by comparing the results to that of mixtures with w/c=0.50. It should be noted that all cement pastes incorporating chemical admixtures were made with a w/c of 0.35. The rheological properties of the various cement pastes were investigated in detail at a moderate temperature of 20°C and high temperatures of 40 and 45°C.

Chemical Admixtures

Five different liquid chemical admixtures were used:

1. Glucofc-based water-reducing and retarding admixture (WRR) that meets ASTM C 494 (Standard Specification for Chemical Admixtures for Concrete) requirements for Type B retarding and Type D water-reducing admixtures. This admixture is intended to simultaneously delay the setting time of concrete and reduce the amount of mixing water required to get a designated slump value [15]. It is believed to counteract the accelerating effect of temperature on cement hydration and improve cement paste rheological properties, which reduces the rate of slump loss of concrete [15,16]. Five dosages of WRR (0.3, 0.7, 1.2, 2.5, and 3.5 % by mass of cement) were used in this study.
2. Polycarboxylate-based mid-range water-reducing admixture (MRWR) which meets ASTM C 494 requirements for Type A water-reducing admixture. Polycarboxylate is a synthetic organic polymer bearing carboxylic acid groups [12]. Five dosages of MRWR (0.3, 0.7, 1.2, 2.5, and 3.5 %) were used.
3. Polycarboxylate-based high-range water-reducing admixture (PHRWR) meeting ASTM C 494 requirements as a Type A water-reducing and Type F high-range water-reducing admixture. Three dosages of PHRWR (0.3, 0.7, and 1.2 %) by mass of cement were used in this study.
4. Naphthalene sulfonate-based high-range water-reducing admixture (SHRWR) which complies with ASTM C 494 Type F high-range water-reducing admixture. Six dosages of SHRWR (0.3, 0.7, 1.2, 2.5, 3.5, and 4.5 %) were used in this study to investigate its effect on the rheological properties of cement paste at high temperature.
5. Melamine-based high-range water-reducing admixture (MHRWR) which complies with ASTM C 494 Type F high-range water-reducing admixture. Six dosages of MHRWR (0.3, 0.7, 1.2, 2.5, 3.5, and 4.5 %) by mass of cement were used.

Mixing Cement Pastes

A high-shear mixer with three variable speeds was used to adequately mix the cement paste components (Fig. 1(*a*)). The mixer consists of a bowl and a vertical shaft with two blades at two vertical levels. First,
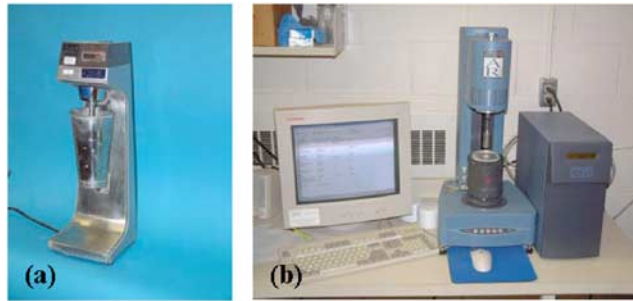
FIG. 1—*Illustration of (a) cement paste mixer, and (b) rheometer used with coaxial cylinder geometry.*

the mixing water was poured into the mixing bowl. Using a needle, the specified quantity of liquid admixture was injected into the mixing water. Then the weighed quantity of cement powder was added to the water and manually stirred for one minute. The cement paste was subsequently mixed for one minute at low speed, then at high speed for another minute. The mixer was stopped for 1.5 min, during which the bowl was scraped with a rubber paddle to ensure homogeneity. Mixing resumed for another minute at high speed. The total time between the beginning of mixing and the start of rheological tests was seven minutes for all cement pastes. This mixing procedure was strictly followed for all cement pastes to avoid the effects of exogenous variables on the results [17,18].

Rheometer

An advanced rheometer (TA-Instruments AR 2000) was used throughout this investigation to measure the shear stress-strain rate data and consequently the rheological properties of cement pastes (Fig. 1(*b*)) [19]. The rheometer has an advanced system for temperature control in the range of −5 to 100°C. Instrument calibration was done using a certified standard Newtonian oil with a known viscosity of 1.40 Pa·s. The measured yield stress was zero and viscosity was 1.42 Pa·s with an error of 1.4 %, which is less than the tolerated error of 4 % specified by the manufacturer.

The geometry of the test accessory has a significant influence on the measured rheological properties of cement paste [20]. The coaxial concentric cylinder geometry was considered suitable for this study and was thus used throughout this investigation. This geometry consists of a cylinder with a conical end that rotates inside a cylinder with a central fixed hollow. The gap between the rotating shaft and the hollow is 1 mm. The gap between the head of the conical end and the bottom of the hollow was set at 0.5 mm and kept constant for all experiments. The rheometer has an auto gap adjustment system which compensates for the expansion of the stainless steel coaxial cylinder when a wide temperature range is applied during an experiment, thus ensuring the gap to remain constant. To keep the w/c constant and prevent evaporation of water from tested cement paste samples due to temperature rise, a solvent trap cover was used.

The rheometer is computer-controlled and equipped with a rheological data analysis software, which can fit the shear stress-strain rate data to several rheological models (e.g., Newtonian, Bingham, Herchel-Bulkley, Caisson, Modified Bingham, Sisko, and Williamson). The Bingham model was used throughout this study to calculate cement paste rheological properties, i.e., yield stress, viscosity, and thixotropy. It is however, understood that rheological data estimated may depend on the rheological model [21–23].

Testing Procedure

After mixing, the cement paste sample was placed in the gap space of the coaxial cylinder. First, temperature was adjusted to the required level over one minute. Then, the cement paste sample was presheared at 70 s^{-1} for two minutes in order to break down the structure of the cement paste sample, creating uniform conditions before testing [24]. The preshearing procedure was kept constant for all tested samples. Subsequently, a continuous sweep shear rate was applied by increasing the shear rate from 0 to 50 s^{-1} to produce the up-curve. The cement paste was maintained 15 s at a shear rate of 50 s^{-1}, and then the sample was sheared from 50 s^{-1} to 0 s^{-1} to produce the down-curve. This procedure allowed producing a hyster-
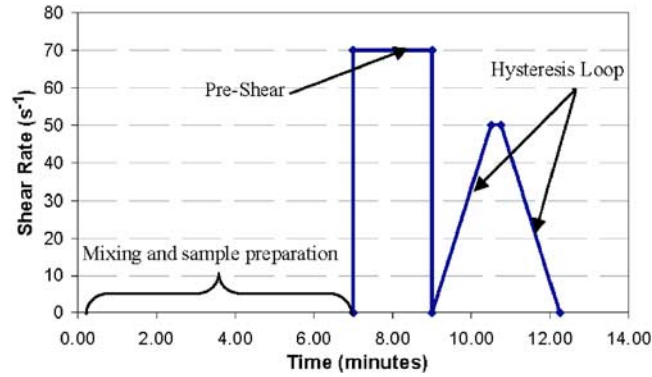
FIG. 2—*Shear rate history used in rheological tests.*

esis loop, which is also used to characterize the thixotropy of cement paste [25]. A schematic representation of the testing procedure is illustrated in Fig. 2.

Rheological Parameters

Generally, cement paste is believed to follow a Bingham behavior, which is represented by the following equation:

$$\tau = \tau_0 + \mu_p \gamma \tag{1}$$

where τ, τ_0, μ_p, and γ are the shear stress, yield stress, plastic viscosity, and shear rate, respectively.

The yield stress is the energy required for the cement paste to start flowing. It can be identified by the intercept of the flow curve (shear rate versus shear stress) with the shear stress axis. After overcoming the yield stress, viscosity indicates how the material can flow. Plastic viscosity is the slope of the fitted straight line of the flow curve to the Bingham model, and the apparent viscosity is the ratio between shear stress and shear rate at each shear rate on the flow curve. Therefore, the apparent viscosity at a specific shear rate is the slope of the flow curve at this point.

The yield stress and plastic viscosity were calculated from the shear rate-shear stress down curve using the Bingham model. The down-curve was adopted because it better fits to the Bingham equation than the up-curve [25,26]. When a cement paste is sheared from 0 to 50 s^{-1}, breakdown in its structure occurs. Thus, the down-curve (unloading) will not usually follow the same path as the up-curve (loading). The down-curve is normally lower in shear stress values than that for the up-curve. Figure 3 shows a typical hysteresis loop for cement paste at high temperature. It can be observed that the down-curve (unloading) became higher than the up-curve during the loading process, which is contrary to normal hysteresis behavior of cement paste at lower temperature. This reverse hysteresis behavior in cement paste was also observed elsewhere [25], and is sometimes called anti-thixotropy or rheopexy [27].
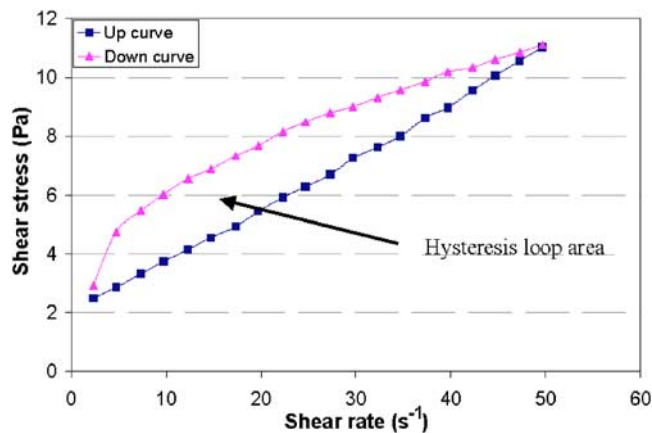
FIG. 3—*Typical hysterersis loop for cement paste at high temperature.*

TABLE 2—*Repeatability of rheological measurements (cement pastes with w/c = 0.5).*

Temperature °C	Plastic Viscosity (Pa·s)			Yield stress (Pa)		
	Measured	Average	Standard Deviation	Measured	Average	Standard Deviation
20	0.27	0.28	0.02	6.41	6.48	0.15
	0.25			6.47		
	0.26			6.76		
	0.29			6.55		
40	0.30	0.29	0.02	7.17	7.40	0.22
	0.26			7.32		
	0.28			7.68		
	0.31			7.50		
45	0.52	0.42	0.04	8.51	8.19	0.32
	0.47			7.76		
	0.45			8.32		
	0.42			8.15		

The reverse hysteresis loop indicates that the structure of the material stiffens as it is sheared at high temperature due to the mechanism of thixotropy build-up [26], likely as a result of accelerated hydration. The area enclosed between the up and down curves was calculated and used to assess the degree of thixotropy [25,26]. In this study, negative thixotropy indicates the normal hysteresis behavior of cement paste, while positive thixotropy refers to the reverse hysteresis behavior.

Analysis of Results

Reliability of Rheometer at Different Temperatures

For further rheometer calibration and to ensure statistical repeatability of results, three sets (each set consists of four cement paste samples prepared at a w/c of 0.50), were tested at three different temperatures, i.e., 20, 40, and 45°C. A new cement paste mixture was used for replicating each test since rheological properties of cement paste are time, temperature, and shear history dependent. As shown in Table 2, the averages of the measured plastic viscosities of the cement pastes at 20, 40, and 45°C were 0.28, 0.29, and 0.42 Pa·s, respectively, with standard deviations of 0.02, 0.02, and 0.04. The averages of the measured yield stress values were 6.48, 7.40, and 8.19 Pa with standard deviations of 0.15, 0.22, and 0.32 Pa at temperatures of 20, 40, and 45°C, respectively. The standard deviation values are relatively small, which confirms that the experimental procedure and the rheometer can produce repeatable measurements with acceptable accuracy.

Furthermore, it can be observed from the results that the yield stress and plastic viscosity values increased with the increase of temperature for both cement pastes with w/c=0.35 and w/c=0.50 (Fig. 4). This is likely due to the increase in the rate of hydration of cement at higher temperature. The increase of the yield stress between 20 and 40°C was less significant than that between 40 and 45°C (Fig. 4(*a*)). This suggests that the increase of yield stress versus temperature is not linear, which is in agreement with findings of Soroka [28] who observed that the rate of slump loss increased with temperature. Similar to yield stress, the rate of increase in plastic viscosity between 40 and 45°C was higher than that between 20 and 40°C (Fig. 4(*b*)). It can be further observed that the rate of increase of yield stress and plastic viscosity for cement pastes with w/c=0.35 was higher than that for cement pastes with w/c=0.50, especially when temperature exceeded 40°C. Figure 4 also shows that when the w/c increased, the values of yield stress and plastic viscosity increased, likely due to the increase in the volume fraction of solids with the decrease of the w/c.

Effect of Admixtures on Yield Stress of Cement Paste at High Temperature

The effect of various admixtures on the yield stress of cement paste at different temperatures is presented in Fig. 5. A different scale is used for the figure presenting results for the WRR due to the much higher yield stress values observed. Figure 5(*a*) illustrates yield stress values measured for cement pastes incorporating various dosages of a water-reducing and retarding admixture (WRR) at different temperatures. It
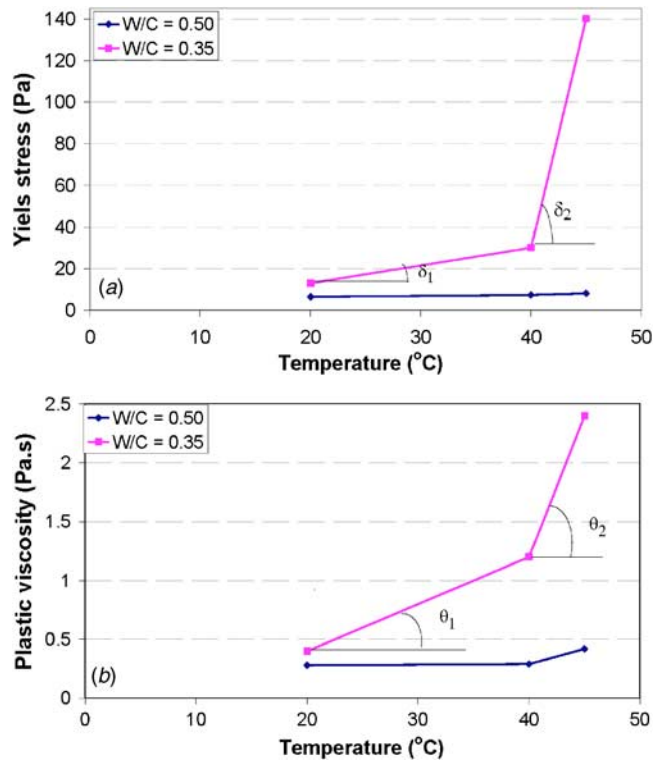
FIG. 4—*Effect of temperature on rheology of cement paste (a) yield stress, (b) plastic viscosity.*

can be observed that yield stress values generally decreased with the increase of the WRR dosage, and increased significantly with temperature increase. The rate of increase in yield stress became much higher when temperature exceeded 40°C, but this increase was less significant at high WRR dosages. For example, at a dosage of 0.3 % the increase in yield stress between 40 and 45°C was about tenfold its value between 20 and 40°C, whereas at a dosage of 2.5 %, the increase in yield stress between 40 and 45°C was only double its value between 20 and 40°C. Although the increase of WRR dosage from 0.7 to 2.5 % reduced the yield stress value at 45°C significantly, the difference in yield stress values for cement paste at 40 and 45°C was still high at about threefold its value between 20 and 40°C. At a higher WRR dosage of 3.5 %, the yield stress of cement paste at high temperature dropped significantly and approached its value at the moderate temperature of 20°C (Fig. 5(*a*)). Additionally, the saturation dosage at 20 and 40°C was comparable at about 1.2 %. However, no saturation dosage was reached when temperature was higher (45°C) even when the dosage was 2.5 to 3.5 %.

In Fig. 5(*b*), the effect of a mid-range water-reducing admixture (MRWR) on the yield stress is presented. At 20°C, yield stress decreased with the increase of MRWR dosage and reached a saturation dosage at about 1.2 %. At 40°C, no evident effect of the change of the MRWR dosage was observed below a dosage of 2.5 %, and then yield stress started to decrease beyond this dosage. At a dosage of 3.5 %, yield stress became lower than the corresponding value at 20°C. At 45°C, yield stress steeply decreased with increasing MRWR dosage and again reached a value less than that at 20°C at a dosage of 3.5 %. It is observed that the MRWR admixture prevented yield stress from escalating to very high values at 45°C, in contrast with the case of the WRR admixture.

The effect of the PHRWR dosage on yield stress with variation of temperature is presented in Fig. 5(*c*). It can be observed that yield stress at low PHRWR dosage (0.3 %) increased significantly with temperature. The difference in yield stress values between 40 and 45°C was about double the corresponding value between 20 and 40°C. At low dosages, the PHRWR could not apparently offset the acceleration of hydration due to the increase of temperature. However, an increased PHRWR dosage seemed to mitigate the acceleration of hydration due to higher temperature, and even neutralized it at a high dosage of 1.2 % since yield stress at the various temperatures approached a value of zero.

In Fig. 5(*d*), the effect of the naphthalene sulfonate-based HRWR admixture on yield stress of cement paste at different temperatures is illustrated. The yield stress initially increased with higher SHRWR dosage. After a threshold dosage (around 1.2 % at 40 and 45°C and 0.7 % at 20°C), yield stress started to
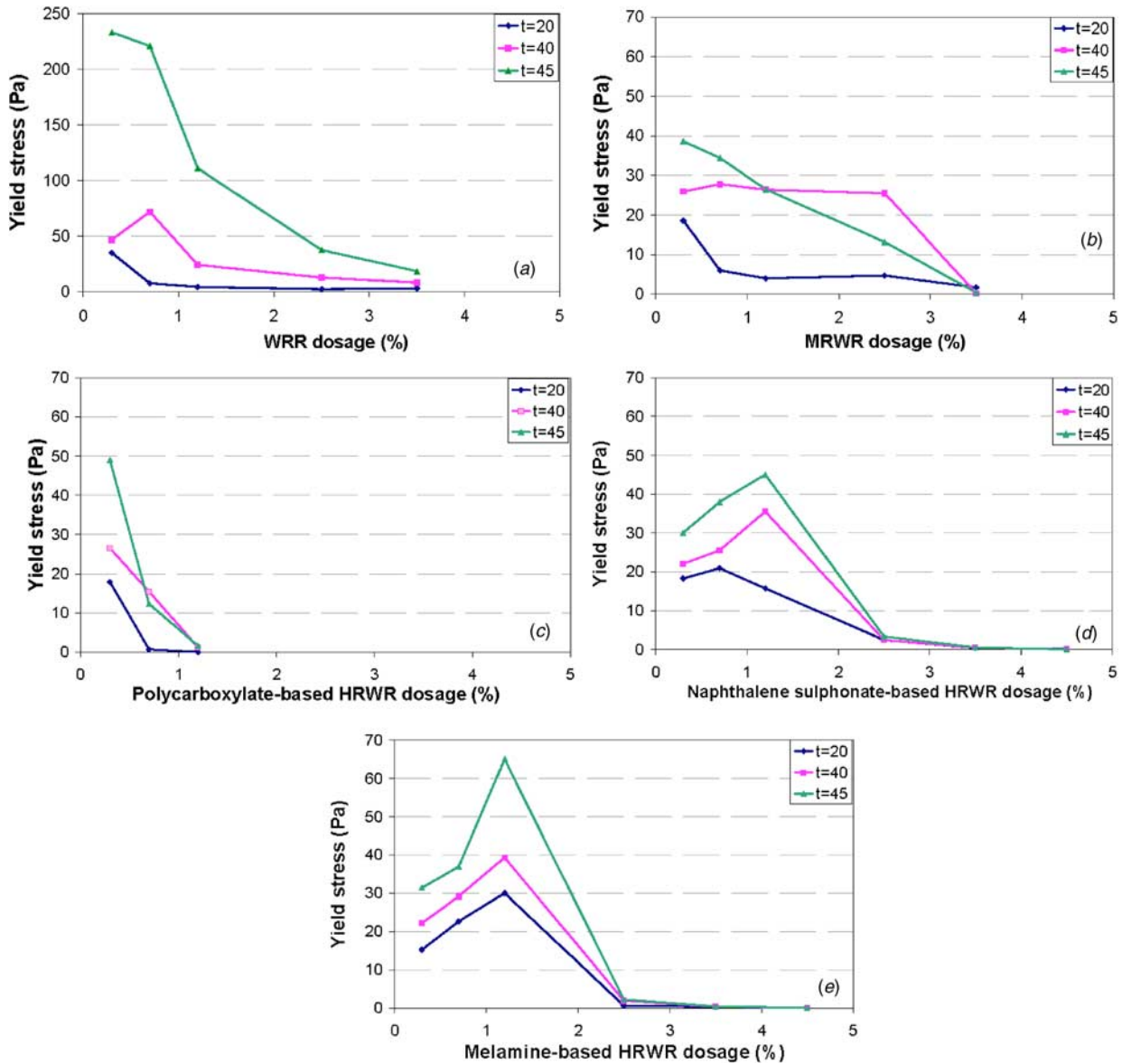
FIG. 5—*Yield stress of cement paste at various temperatures and different dosages of admixtures (a) WRR, (b) MRWR, (c) PHRWR, (d) SHRWR, and (e) MHRWR (w/c =0.35; admixture dosage is in % of cement mass).*

drop significantly. This indicates that at low admixture dosages and high temperatures, the SHRWR was not effective and rather acted as an accelerator. This behavior of the SHRWR was also documented by other researchers [12,29].

As shown in Fig. 5(e), yield stress also initially increased with temperature and MHRWR dosage up to about 1.2 %, and then it started to decrease steeply at higher dosages until it reached a plateau (saturation dosage) at about a dosage of 3.5 %, where no further decrease in yield stress could be achieved. MHRWR acted as an accelerator at low dosage where it enhanced yield stress likely via acceleration of hydration at increased temperature, and it acted as a retarder at high dosages where it reduced yield stress and effectively offset the acceleration of hydration at high temperature. It was documented by others [12] that MHRWR acted as an accelerator below a dosage of 2 % and as a retarder above this dosage.

Effect of Admixtures on Viscosity of Cement Paste at High Temperature

Figure 6(a) illustrates the variation of plastic viscosity at different temperatures for cement pastes incorporating various dosages of WRR. Generally, plastic viscosity decreased significantly with the increase of the WRR dosage but reached a threshold value at a dosage of 0.7 % at 20, 40, and 45°C beyond which no
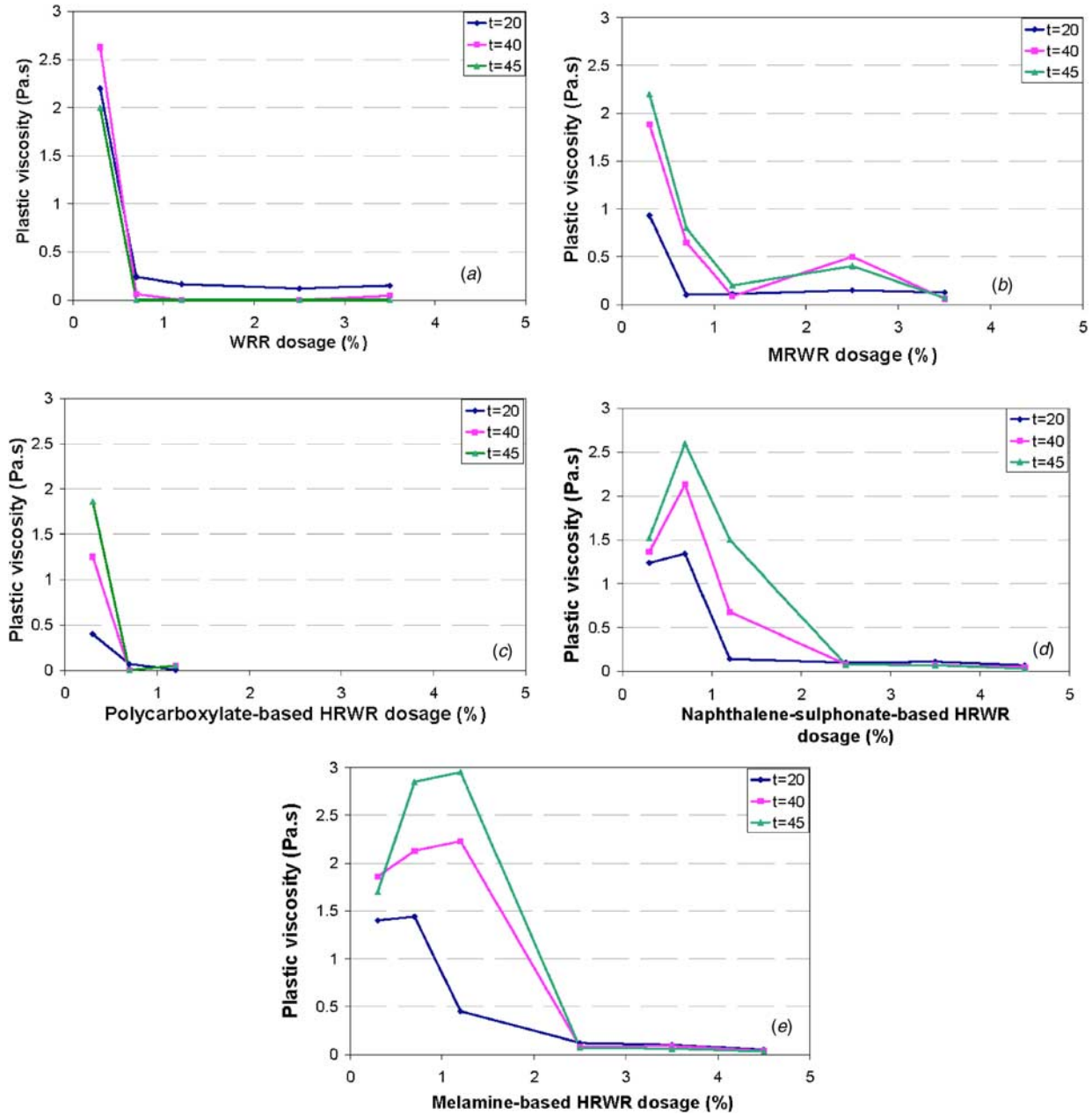
FIG. 6—*Plastic viscosity of cement paste at various temperatures and different dosages of admixtures (a) WRR, (b) MRWR, (c) PHRWR, (d) SHRWR, and (e) MHRWR (w/c = 0.35; admixture dosage is in % of cement mass).*

significant reduction in plastic viscosity could be achieved. Tables 3 and 4 show that there were significant changes in the apparent viscosity at low and high shear rate when the temperature and WRR dosage changed. Generally, the apparent viscosity increased with the increase of temperature, and decreased when the WRR dosage increased. It can be further observed that the rate of increase in apparent viscosity at both high and low shear rate was much higher at a higher temperature for all cement pastes incorporating different WRR dosages. For instance, the apparent viscosity at low shear rate (5 s^{-1}) for cement paste at a WRR dosage of 0.3 % increased fourfold between 40 and 45°C, while the corresponding value at 40°C was less than double that at 20°C.

It can be argued that plastic viscosity measured from the down-curve of the hysteresis loop does not always truly represent the material property. This is because the slope of the line generated by fitting a cement paste flow curve to the Bingham model depends on the error of the fit, which is in some cases high, a behavior also observed by Saak [25]. In this study, plastic viscosity was measured and analyzed because

TABLE 3—Apparent viscosity at low shear rate (5 s⁻¹) for cement pastes made with different admixtures (w/c = 0.35).

% of Cement Mass	T=20°C					T=40°C					T=45°C				
	WRR[a]	MRWR[a]	PHRWR[a]	SHRWR[a]	MHRWR[a]	WRR	MRWR	PHRWR	SHRWR	MHRWR	WRR	MRWR	PHRWR	SHRWR	MHRWR
0.3	7.80	4.40	3.60	4.36	3.85	10.70	5.90	5.50	4.12	5.40	47.00	8.00	9.60	4.40	7.40
0.7	1.70	1.40	0.22	5.05	5.20	5.34	5.50	3.15	5.88	6.75	33.80	6.63	2.58	9.33	7.62
1.2	1.06	0.96	0.05	3.40	5.80	4.20	4.80	0.28	6.50	8.93	24.54	4.92	0.37	8.80	12.63
2.5	0.72	1.03		0.62	0.25	2.4	5.50		0.60	0.50	8.25	2.70		0.75	0.50
3.5	0.55	0.45		0.15	0.10	1.65	0.06		0.18	0.10	4.10	0.18		0.13	0.11
4.5				0.10	0.05				0.06	0.04				0.03	0.04

[a]WRR: water-reducing and retarding admixture, PHRWR: polycarboxylate-based high-range water-reducing admixture, MRWR: mid-range water-reducing admixture, SHRWR: naphthalene sulfonate-based high-range water-reducing admixture, and MHRWR: melamine-based high-range water-reducing admixture.

TABLE 4—Apparent viscosity at high shear rate (45 s^{-1}) for cement pastes made with different admixtures (w/c = 0.35).

% of Cement Mass	T=20°C					T=40°C					T=45°C				
	WRR	MRWR	PHRWR	SHRWR	MHRWR	WRR	MRWR	PHRWR	SHRWR	MHRWR	WRR	MRWR	PHRWR	SHRWR	MHRWR
0.3	2.77	1.30	0.73	1.55	1.66	3.56	2.32	1.73	1.63	2.20	7.00	2.60	2.74	1.80	2.30
0.7	0.36	0.24	0.09	1.70	1.80	1.75	1.17	0.32	2.50	2.58	4.00	1.20	0.25	3.40	3.40
1.2	0.24	0.20	0.04	0.48	1.04	0.45	0.65	0.08	1.32	2.20	2.12	0.55	0.08	1.50	3.63
2.5	0.21	0.22		0.15	0.13	0.28	0.50		0.13	0.13	0.63	0.28		0.15	0.12
3.5	0.17	0.16		0.08	0.09	0.21	0.12		0.06	0.05	0.35	0.06		0.03	0.04
4.5				0.07	0.05				0.05	0.04				0.03	0.03

WRR: water-reducing and retarding admixture, PHRWR: polycarboxylate-based high-range water-reducing admixture, MRWR: mid-range water-reducing admixture, SHRWR: naphthalene sulfonate-based high-range water-reducing admixture, and MHRWR: melamine-based high-range water-reducing admixture.

it is generally used to create mechanical models for the deformation behavior of cement paste since it is very difficult to rely on apparent viscosity measurements at each shear rate point to formulate such models [21].

Figure 6(b) shows the effect of incorporating a mid-range water-reducing admixture (MRWR) on the plastic viscosity of cement pastes at various temperatures. It can be observed that at low dosages (0.3 and 0.7 %) plastic viscosity increased at a relatively constant rate when temperature increased. Moreover, plastic viscosity decreased when the dosage of MRWR increased and reached a low value that was independent of temperature at a dosage of 1.2 %, likely due to the retarding effect of MRWR at high dosage. Some increase in plastic viscosity was observed for a dosage of 2.5 % at 40 and 45°C. Since this behavior was not observed for the apparent viscosity, it could be attributed to the error associated with the fitting of cement paste flow curve to the Bingham model as discussed previously. Similar to plastic viscosity, the apparent viscosity at high and low shear rates increased with temperature and decreased when the MRWR dosage increased (Tables 3 and 4). It is further observed from Table 3 that at 40°C and below a dosage of 2.5 %, the apparent viscosity at low shear rate of cement pastes incorporating MRWR did not show any trend (increase or decrease), but decreased steeply beyond this dosage. A similar behavior was also observed for yield stress. This indicates that it may be necessary to consider the specific site temperature when designing concrete mixtures incorporating MRWR for hot weather conditions.

Figure 6(c) shows the effect of the polycarboxylate-based HRWR admixture on the plastic viscosity of cement pastes at different temperatures. At low PHRWR dosage (0.3 %), it can be observed that plastic viscosity increased when temperature increased due to accelerated hydration reactions. At higher dosage (0.7 and 1.2 %), plastic viscosity dropped significantly at all temperatures. In general, the apparent viscosity decreased with an increase of the PHRWR dosage for both low and high shear rates (Tables 3 and 4). Due to shear thinning behavior, the apparent viscosity at high shear rate was smaller than that at lower shear rate for a specific temperature and PHRWR dosage. Regardless of the shear rate, the apparent viscosity at 20°C approached a zero value at a PHRWR dosage of 1.2 % (Tables 3 and 4). At 40 and 45°C and PHRWR dosage beyond 0.7 %, apparent viscosity measurements at each PHRWR dosage were comparable. From Fig. 6(c) and Tables 3 and 4, it appears that the apparent viscosity varied with temperature and PHRWR dosage in a manner generally similar to that of plastic viscosity.

In Fig. 6(d) the effect of the naphthalene sulfonate-based HRWR on plastic viscosity is presented. There appeared to be an initial increase in plastic viscosity with increasing SHRWR dosage and temperature until a threshold dosage of about 0.7 %, beyond which plastic viscosity decreased with increasing SHRWR dosage. When the SHRWR dosage and temperature varied, the effect on apparent viscosity at both high and low shear rates was similar to that observed for plastic viscosity (Tables 3 and 4). Again, as the SHRWR dosage increased, the apparent viscosity increased until a dosage of 0.7 and 1.2 % for high and low shear rates, respectively, after which it started to decrease. Moreover, the apparent viscosity at each SHRWR dosage increased when temperature increased. The value of apparent viscosity at each SHRWR dosage and temperature decreased at higher shear rates.

As shown in Fig. 6(e), plastic viscosity increased with temperature and with the MHRWR dosage up to a threshold level of 1.2 % for temperatures of 40 and 45°C, and 0.7 % for 20°C. Then, it started to decrease steeply until it reached a plateau (saturation dosage). The MHRWR dosage also affected the apparent viscosity; an increase in dosage up to 1.2 % increased the apparent viscosity at both low and high shear rates. However, the apparent viscosity decreased steeply beyond a MHRWR dosage of 1.2 %.

Effect of Various Chemical Admixtures on Thixotropy

Figure 7(a) shows the effect of WRR on thixotropy of cement pastes. Thixotropy increased dramatically when temperature increased, especially when temperature exceeded 40°C. Thixotropy was generally higher at a WRR dosage of 0.7 % than that at a dosage of 0.3 %, perhaps because the amount of stiffening upon relaxation for a dosage of 0.7 % was higher due to a more effective particle dispersion than that for a dosage of 0.3 %. Beyond a dosage of 0.7 %, thixotropy values started to decrease gradually with the increase of the WRR dosage. Furthermore, the difference in thixotropy values between 40 and 45°C for all WRR dosages were much higher than that between 20 and 40°C.

In Fig. 7(b) thixotropy measurements for cement pastes made with a mid-range water-reducing admixture (MRWR) are illustrated. At 20°C, thixotropy had negative values, indicating that the hysteresis loop had a regular behavior. At high temperature (40 and 45°C), thixotropy increased with the dosage of
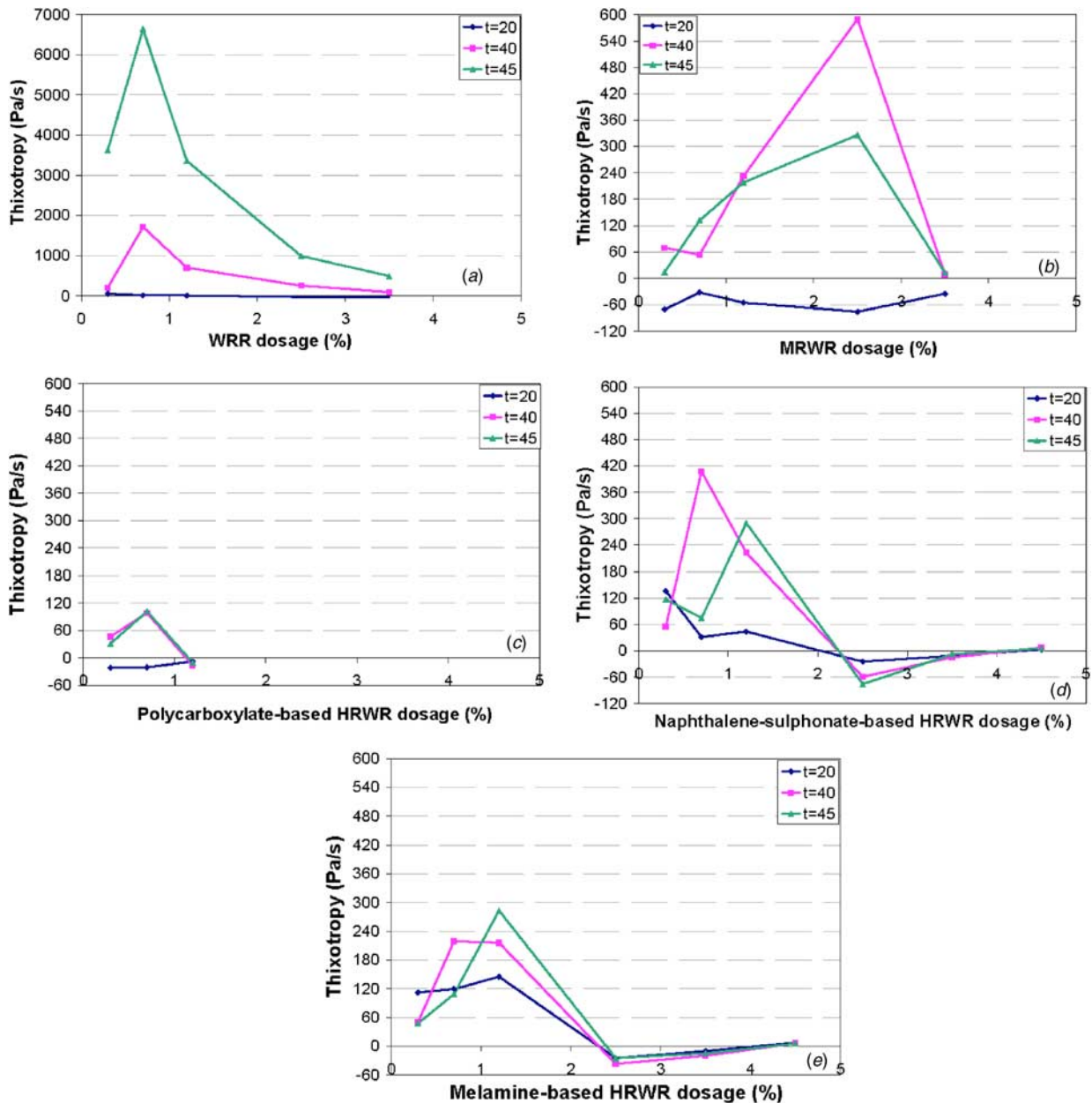
FIG. 7—*Thixotropy of cement paste at various temperatures and different dosages of admixtures (a) WRR, (b) MRWR, (c) PHRWR, (d) SHRWR, and (e) MHRWR (w/c = 0.35; admixture dosage is in % of cement mass).*

MRWR up to a dosage of 2.5 % at which it started to drop and reached a low value at a dosage of 3.5 %. This indicates that low dosages of the MRWR could not mitigate the increase in stiffening of cement pastes at high temperature, while it could achieve this goal at a high dosage (3.5 %). It can be further observed that at a dosage of 2.5 %, the thixotropy value at 40°C was higher than that at 45°C, which is consistent with that of yield stress.

The thixotropy behavior for cement pastes incorporating the polycarboxylate-based HRWR is presented in Fig. 7(c). Due to its effective dispersing mechanism, PHRWR could effectively mitigate the build up of cement paste structure as a result of temperature increase, and thixotropy values were generally lower than those of mixtures incorporating the WRR and MRWR. At 20°C, thixotropy reached negative values for all PHRWR dosages indicating that cement paste thixotropy turned back to its normal hysteresis behavior. At high temperatures of 40 and 45°C, thixotropy increased slightly when the admixture dosage increased from 0.3 to 0.7 %. However, thixotropy became negative for both temperatures when the

PHRWR dosage exceeded 1.2 %, indicating that the hysteresis behavior at high temperature became normal and that no significant effect of high early stiffening of cement paste is taking place.

The thixotropy behavior of cement pastes made with SHRWR is presented in Fig. 7(*d*). At 20°C, thixotropy decreased with increasing SHRWR dosage and reached negative values (normal behavior) beyond a dosage of about 2 %. Thixotropy increased dramatically up to a SHRWR dosage of around 1.2 and 0.7 % for 40 and 45°C, respectively, and then decreased until it reached a negative value at a dosage of about 2 %. Moreover, using high dosages of SHRWR shifted the reverse hysteresis behavior of cement paste back to its normal and delayed the stiffening of cement paste.

The effect of the MHRWR on thixotropy is shown in Fig. 7(*e*). It can be observed that thixotropy values increased at all temperatures with the increase of the MHRWR dosage until a threshold dosage of 1.2 % at which thixotropy started to decrease. At a dosage of 2.5 %, thixotropy values became negative indicating that the reverse hysteresis loop has turned back to a regular behavior.

Discussion

Rheological parameters at high temperature for cement pastes made with various dosages of five different admixtures were investigated in this study. Although the effects of plasticizers and temperature on the rheology of cement grouts were investigated previously [30], it was attempted in the current study to determine the rheological properties of cement pastes incorporating various types of chemical admixture that can be used in hot weather concreting. Moreover, a larger range of temperature was investigated in this study to cover a wider scope of temperature that can occur in hot weather during placement of concrete.

The effects of various chemical admixtures and temperature on the rheological properties of cement paste were clearly depicted in measured yield stress and apparent viscosity values, especially at low shear rate (5 s^{-1}). It was observed that there was a strong agreement between the behavior and trend of both yield stress and apparent viscosity at low shear rate (5 s^{-1}). Plastic viscosity did not always truly describe the effects of chemical admixtures and temperature on the rheological properties of cement paste at high temperature as discussed earlier. The thixotropy behavior of cement paste at high temperature was also investigated. In general, it was observed that at low dosage of chemical admixtures, thixotropy increased with the increase in temperature. This is due to the build up in the structure of cement paste due to the acceleration of hydration reactions. It was also observed that there was a decrease in thixotropy when the dosage of admixtures increased. This is likely due to the delay in stiffening of cement paste induced by the action of chemical admixtures.

The differences in rheological results observed can be attributed to the various mechanisms by which each admixture affects the behavior of cement paste. The glucofc-based WRR admixture showed a different behavior than that expected. Instead of acting as a retarder at high temperature, it rather behaved as an accelerator. It was observed in previous work [31] that using WRR increased the slump loss when concrete was under prolonged mixing for up to 180 min at temperatures of 21 and 32°C. Meyer and Perenchio [15] investigated the reasons behind the rapid stiffening of cement paste when WRR was incorporated and attributed this behavior to the accelerated hydration of C_3A due to the presence of WRR, resulting in rapid formation of fine ettringite crystals, which connected solid particles together.

Other studies suggested that adsorption could be one of the mechanisms by which WRR operates [12,15,31]. Adsorption of the admixture on the surfaces of unhydrated cement grains forms a barrier preventing water from reacting with cement grains, consequently, delaying the hydration process. A high temperature could break this layer, leading to accelerated hydration. This could be the reason why the WRR failed to operate as a retarder at high temperature. Therefore, it can be suggested that a WRR Type D may act only as a water reducer at high temperature and could lose its retarder quality.

Moreover, lower water content is typically associated with smaller spacing between solid particles in the fresh mixture. Thus, hydration products can easily bridge the space between cement particles due to the proximity of particles, resulting in a faster rate of hydration and stiffening is brought about earlier. This could be an additional reason why the WRR Type D behaved as an accelerator at high temperature, which suggests that using WRR Type D at very high temperature is not recommended.

The effect of the naphthalene sulfonate and melamine-based HRWR admixtures was found to be dosage-dependent; they tended to act as accelerators at low dosages and as retarders at high dosages. This

behavior was discussed by Ramachandran et al. [12]. It was found that at a dosage less than 2 %, both MHRWR and SHRWR accelerated the hydration of C_3A and C_3S, while when the dosage exceeded 2 %, they retarded the hydration of C_3A and C_3S. Therefore, it is argued that at high temperatures, these admixtures could be used effectively only at high dosages.

Due to its effective dispersing mechanism, the polycarboxylate-based HRWR deflocculates cement flocks and frees the entrapped water to fluidize the cement paste [12]. Therefore, it effectively enhanced the rheological properties of cement pastes at high temperature, and this admixture seemed to be effective for concrete in hot weather conditions.

The recommended dosages by the manufacture of the studied admixtures are 0.20 % ±0.07 %, 0.20 to 0.78 %, 0.2 to 1 %, 0.65 to 1.6 %, and 0.6 to 1.5 % for WRR, MRWR, PHRWR, SHRWR, and MHRWR, respectively. By comparing these dosages with the results presented in this study, it can be observed that the recommended dosages are below those that seemed effective at high temperature, except for the PHRWR which had a reasonable recommended range.

It should be noted that the effect of these admixtures on the rheology of cement paste at high temperature was investigated immediately after mixing. Their time dependent behavior is critical for their performance in hot weather concreting. Work in progress will focus on the combined effect of temperature and time on the performance of these admixtures to formulate more realistic recommendations for field practice.

Further research is also needed to investigate the effect of possible hybrid blends of these admixtures at high temperature versus time and to assess compatibility between various admixtures and a wide scope of cementitious blends to optimize binder-admixture formulations for effective use in hot weather concreting applications. Such investigation should go beyond the classic flow behavior to address volume change at high temperature and long-term mechanical strength and durability to make final recommendations for hot weather concreting.

Conclusions

The effects of various chemical admixtures on the rheological properties of cement paste at high temperature were investigated in this study. Five admixtures were used including a glucofc-based water-reducing and retarding admixture (WRR), a polycarboxylate-based mid-range water-reducing admixture (MRWR), a polycarboxylate-based high-range water-reducing admixture (PHRWR), a naphthalene sulfonate-based high-range water-reducing admixture (SHRWR), and a melamine-based high-range water-reducing admixture (MHRWR). Various cement pastes were made incorporating different dosages of the admixtures. Their rheological properties were investigated at 20, 40, and 45°C. The following conclusions can be drawn:

- Cement paste at high temperature can have a reverse hysteresis behavior.
- Both yield stress and viscosity increased nonlinearly with temperature.
- The WRR used in this study acted as an accelerator at high temperature and is not recommended for concrete in hot weather conditions.
- The MRWR improved the rheological properties of cement paste at high temperature only at a dosage beyond 2.5 % where both yield stress and apparent viscosity continuously decreased with the increase of MRWR dosage, while thixotropy approached a value of zero at a dosage of 3.5 %.
- The PHRWR effectively improved the rheological properties of cement paste at high temperature.
- SHRWR and MHRWR behaved as accelerators at low dosages but improved the rheological properties of cement paste at high dosages.
- Further research is needed to investigate the effects of these admixtures versus time and temperature, and to examine possible hybrid blends of these admixtures and their compatibility with binders used in hot weather concreting.
- It should be emphasized that the findings of this study are valid for the admixtures used herein. Other admixtures, even from the same category, may exhibit different behavior, and thus should be investigated to validate the current results.

References

[1] Soroka, I. and Ravina, D., "Hot Weather Concreting with Admixtures," *Cem. Concr. Compos.*, Vol. 20, No. 4, 1998, pp. 129–136.

[2] Thomas, J. J., Rothstein, D., Jennings, H. M., and Christensen, B. J., "Effect of Hydration Temperature on the Solubility Behavior of Ca-, S-, Al-, and Si-Bearing Solid Phases in Portland Cement Pastes," *Cem. Concr. Res.*, Vol. 33, No. 12, 2003, pp. 2037–2047.

[3] Berge, O., "Improving the Properties of Hot-Mixed Concrete Using Retarding Concrete Admixtures," *ACI Journal, Proceedings*, Vol. 73, No. 7, 1976, pp. 394–398.

[4] ACI Committee 308, "Recommended Practice for Hot Weather Concreting," ACI 305R-77, *ACI Manual of Concrete Practice*, American Concrete Institute, Detroit, 1992, Part 2.

[5] El-Rayyes, M. S., "Remedies to Rapid Setting in Hot Weather Concreting," *Proceedings, RILEM Symposium, Admixtures for Concrete*, E. Vazques, Ed., Chapman & Hall, London, 1990, pp. 120–134.

[6] Hasanain, G. S., Khalaf, T. A., and Mahmood, K., "Water Evaporation from Freshly Placed Concrete Surfaces in Hot Weather," *Cem. Concr. Res.*, Vol. 19, No. 3, 1989, pp. 465–475.

[7] Abbasi, F. A., Al-Tayyib, A. J., and Al-Ali, M. B., "Effect of Hot Weather on Strength of Reinforced Concrete Beams," *Cem. Concr. Compos.*, Vol. 14, 1992, pp. 209–221.

[8] Barnes, D. B., Orndorff, L. R., and Roten, E. J., "Low Initial Curing Temperature Improving the Strength of Concrete Test Cylinders," *ACI J.*, Vol. 74, No. 12, 1977, pp. 612–615.

[9] ACI Committee Report 305, "Hot Weather Concreting," *ACI Mater. J.*, Vol. 88, No. 4, 1991, pp. 417–436.

[10] Takeuchi, H., Tsuji, Y., and Nanni, A., "Concrete Precooling Method by Means of Dry Ice," *Concr. Int.*, Vol. 15, No. 11, 1993, pp. 52–56.

[11] Kurita, M., Goto, S., Minegishi, K., Negami, Y., and Kuwhara, T., "Precooling Concrete Using Frozen Sand," *Concr. Int.*, Vol. 12, No. 6, 1990, pp. 60–65.

[12] Ramachandran, V. S., Malhotra, V. M., Jolicoeur, C., and Spiratos, N., "Superplasticizers: Properties and Applications in Concrete," *Materials Technology Laboratory, CANMET, Natural Resources Canada*, Ottawa, Ontario, 1997, pp. 43–150.

[13] Ravina, D., "Retempering of Prolonged Concrete with Admixtures in Hot Weather, *ACI J.*, Vol. 72, No. 6, 1975, pp. 291–295.

[14] Hampton, J. S., "Extended Workability of Concrete Containing High-Range Water-Reducing Admixtures in Hot Weather," *Developments in the Use of Superplasticizers*, ACI Spec. Publ. SP 68, Detroit, 1981, pp. 409–422.

[15] Meyer, L. M. and Perenchio, W. F., "Theory of Concrete Slump Loss as Related to the Use of Chemical Admixtures," *Concr. Int.*, Vol. 1, No. 8, 1979, pp. 36–43.

[16] Fattuhi, N. I., "Influence of Temperature on the Setting of Concrete Containing Admixtures," *Constr. Build. Mater.*, Vol. 2, No. 1, 1988, pp. 27–30.

[17] Roy, D. and Asaga, K., "Rheological Properties of Cement Mixes: III. The Effects of Mixing Procedures on Viscometric Properties of Mixes Containing Superplasticizers," *Cem. Concr. Res.*, Vol. 9, No. 6, 1979, pp. 731–739.

[18] Williams, A. D., Saak, W. A., and Jennings, H. M., "The Influence of Mixing on the Rheology of Fresh Cement Paste," *Cem. Concr. Res.*, Vol. 29, No. 9, 1999, pp. 1491–1496.

[19] TA Rheology Advanced Data Analysis, Product- V 3.0.1, New Castle (DE), USA (2001) http//www.tainst.com

[20] Rahman, M. A. and Nehdi, M., "Effect of Geometry, Gap, and Surface Friction of Test Accessory on Measured Rheological Properties of Cement Paste," *ACI Mater. J.*, Vol. 100, No. 4, 2003, pp. 331–339.

[21] Nehdi, M. and Rahman, M. A., "Estimating Rheological Properties of Cement Pastes Using Various Rheological Models for Different Test Geometry, Gap and Surface Friction," *Cem. Concr. Res.*, Vol. 34, No. 11, 2004, pp. 1993–2007.

[22] Papo, A., "Rheological Models for Cement Pastes," *Mater. Struct.*, Vol. 15, No. 3, 1988, pp. 511–519.

[23] Malek, R. I. A. and Roy, D. M., "Modeling the Rheological Behavior of Cement Pastes. A Review,"

Advances in Cementitious Materials, S. Mindess, Ed., The American Ceramic Society, Vol. 16, 1991, pp. 31–40.

[24] Saak, W. A., Jennings, M. H., and Shah, P. S., "The Influence of Wall Slip on Yield Stress and Viscoelastic Measurements of Cement Paste," *Cem. Concr. Res.*, Vol. 31, No. 2, 2001, pp. 205–212.

[25] Saak, W. A., "Characterization and Modeling of the Rheology of Cement Paste: With Application Toward Self-Flowing Materials," Ph.D. Thesis, University of Northwestern, 2000, pp. 97–116.

[26] Eirich, R. F., *Rheology Theory and Applications*, Academic Press, New York and London, 1960, pp. 205–248.

[27] Ferguson, J. and Kemblowski, Z., *Applied Fluid Rheology*, Elsevier Applied Science, London and New York, 1991, pp. 209–210.

[28] Soroka, I., *Concrete in Hot Environments*, E & FN Spon, London, 1993, pp. 69–99.

[29] Szecsy, S. R., "Concrete Rheology," Ph.D. Thesis, University of Illinois at Urban-Champaign, 1997, pp. 125–148.

[30] Domone, P. L. and Thurairatnam, H., "The Effect of Water/Cement Ratio, Plasticizers and Temperature on the Rheology of Cement Grouts, *Advances in Cement Research*, Vol. 1, No. 4, 1988, pp. 195–206.

[31] Ravina, D. and Soroka, I., "Slump Loss and Compressive Strength of Concrete Made with WRR and HRWR Admixtures and Subjected to Prolonged Mixing," *Cem. Concr. Res.*, Vol. 24, No. 8, 1994, pp. 1455–1462.