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# Influence of Thixotropy on Stability Characteristics of Cement Grout and Concrete

by Kamal H. Khayat, Mladenka Saric-Coric, and Frank Liotta

The use of viscosity-enhancing admixtures increases the homogeneity of cement-based materials and leads to greater uniformity of hardened properties. These admixtures increase the yield value and viscosity rheological parameters; however, their impacts on enhancing the thixotropic behavior of the cement paste and concrete are unknown. The effect of both classes of admixtures on the rheological parameters can be quite different. Common viscosity-enhancing admixtures function by imparting structure to the liquid phase, whereas thixotropy admixtures function by imparting structure to the solid phase.

The effect of welan gum and cellulose-based viscosity-enhancing admixtures and propylene carbonate (PPC) thixotropic admixture on the performance of cement grout made with a water-cement ratio (w/c) of 0.40 was investigated. The mixtures had equal initial flow-time consistencies and were tested to determine their rheological parameters, thixotropy, bleeding, setting time, heat flux, and strength development. The effect of combined additions of the thixotropic admixture with a low dosage of viscosity-enhancing admixture on slump retention, stability, setting time, and strength development was also evaluated for flowable concrete with a w/c of 0.41.

Grout and concrete mixtures made with the thixotropic admixture exhibited a greater demand for high-range water-reducing admixtures and losses in fluidity than those made with a viscosity-enhancing admixture. The use of PPC led to considerable improvement in time-dependent stability characteristics, including static bleeding and surface settlement. On the other hand, the increase in thixotropy was not effective in improving stability characteristics determined shortly after mixing and prior to the development of thixotropy. This included resistance to pressure filtration and washout. The combined additions of PPC and low concentrations of a cellulose-based viscosity-enhancing admixture were very efficient, however, in enhancing stability compared with similar mixtures made with either admixture. No adverse effects on setting or strength development were observed with these combinations.

**Keywords:** concrete; grout; high-range water-reducing admixture; rheology; thixotropy; viscosity.

## INTRODUCTION

Viscosity-enhancing admixtures (VEAs) are incorporated to improve the ability of highly flowable cement-based materials to maintain homogenous suspension in the plastic stage. Such stability is critical in highly fluid grouts such as those used for injection grouting and grouts employed for sealing post-tensioned structures. High stability is also required to reduce the risk of segregation and flow blockage of self-consolidating concrete. In the case of underwater-cast concrete, it is also essential to secure high stability to minimize the segregation and water dilution that can affect the performance of the hardened material.

High stability can be required soon after mixing where adequate viscosity can be required to ensure homogeneous suspension of material constituents, as in the case of resistance

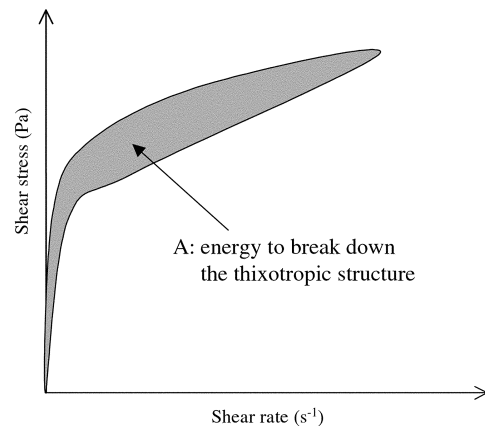


Fig. 1—Flow curve showing thixotropic behavior.

to water dilution of underwater-cast concrete and resistance to segregation during the flow of self-consolidating concrete through restricted spacing. Increased stability may, however, be required over the plastic period where a buildup of viscosity can enhance the resistance of concrete to surface settlement, segregation, and bleeding. A buildup of viscosity, or structure, is possible with the use of a VEA that can increase the viscosity of the liquid phase. A fast buildup of viscosity can be due to a thixotropy whereby the cohesiveness increases with the elapsed time of rest. This can be due to physical effects, chemical effects, or both, associated with cement hydration. The physical explanation relates to a buildup of interparticle friction and cohesion among the various cement particles and admixture molecules.

Thixotropy can be assessed by determining the difference between the ascending and descending legs of the shear stress-shear rate rheograms, as illustrated in Fig. 1. Such hysteresis represents a quantitative measurement of the energy necessary to disturb the structure of a given volume of grout following some period of rest, as noted

$$\text{Area of hysteresis} = \tau \times \gamma \text{ [Pa} \cdot \text{1/s]} = \text{N/m}^2 \times \text{1/s} = \text{Nm/s} \times \text{1/m}^3$$

$$A = \text{work/shear time} \times \text{1/volume} = \text{energy/volume}$$

The potential of a liquid to reestablish its structure and increase its resistance to flow is therefore a measurement of

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its degree of thixotropy. Thixotropic behavior is encountered in some solid-dispersion systems in which physical interactions between various molecules can be high after a certain period of rest, leading to the formation of a gel structure that is highly cohesive despite its high water content. Bond among various molecules leading to a rise in cohesiveness can correspond to hydrogen or ionic bonding, as shown in Fig. 2.<sup>1</sup> Such bond takes place especially at a low shear rate and can be destroyed by mixing the dispersion at a high shear rate. The reagglomeration and reestablishment of the various bonds among adjacent molecules can be established again following a rest period.

Although VEAs increase viscosity, their effects on thixotropy can be quite different. Cellulose-based VEAs and microbial polysaccharides such as welan gum function by occupying volume in the liquid phase and resulting in a thickening of that phase. On the other hand, thixotropic admixtures (such as propylene carbonate [PPC]) function by inducing a network structure in the fluid phase through increased interactions of the solid particles.

PPC, used in this study as a thixotropic admixture, is a liquid cyclic organic carbonate with a water solubility of approximately 8%. Unlike most known VEAs, PPC undergoes a chemical reaction in the aqueous alkaline environment of cement-based materials and rapidly reacts to form propylene glycol and carbonate anion.<sup>2</sup> At typical application temperatures, the half-life for alkaline hydrolysis of PPC is less than one minute.<sup>2</sup> As shown in the structure of the PPC as follows, the PPC hydrolyzes rapidly to propylene glycol and

carbonate. It is unlikely that the PPC itself is responsible for the gel formation. The hydrogens on the propylene glycol hydroxyls can develop hydrogen bond. Since propylene glycol does exhibit the same effect as PPC, it is not responsible alone for the observed effects. While hydrogen bonding is one possible source of the increase in viscosity of cement-based systems, the actual mechanism is probably a combination of effects, including the interaction of the carbonate with the cement particles.

The thixotropic and set-accelerating properties of cyclic organic carbonates such as PPC have been shown in prior research.<sup>3-5</sup> The use of PPC at relatively high dosages (greater than 0.5% by mass of water) can lead to the formation of a gel structure within 10 min following the first contact of the cement with water. A grout mixture containing 0.8% PPC made without any high-range water-reducing admixture (HRWR) and a mixture with 1% PPC made with HRWR were found to lead to the formation of a gel structure shortly after the end of mixing. The fluidity of the resulting thixotropic grout could, however, be reestablished following rigorous mixing.

Limited information exists on the effect of PPC and its addition along with conventional VEAs on the characteristics of cement-based materials. The objective of this study was to evaluate the effect of thixotropy on the stability of cement-based materials. The influence of various combinations of HRWR and VEA in cement grout made with and without the PPC thixotropic admixture on rheology, stability, setting, kinetics of cement hydration, and strength development was investigated.

## SCOPE OF INVESTIGATION

Phase I of this study was undertaken to compare fresh and hardened properties of grout mixtures prepared with different viscosity-enhancing and thixotropic admixture combinations. The HRWR dosage was adjusted to secure similar initial flow consistency. Two mixtures were prepared with conventional VEA (welan gum used in a powder form and a liquid-based cellulose material). The third grout incorporated PPC at a moderate dosage of 0.7% by mass of water. A control grout containing HRWR and no VEA was prepared for the control mixture. The grouts had a fixed water-cement ratio

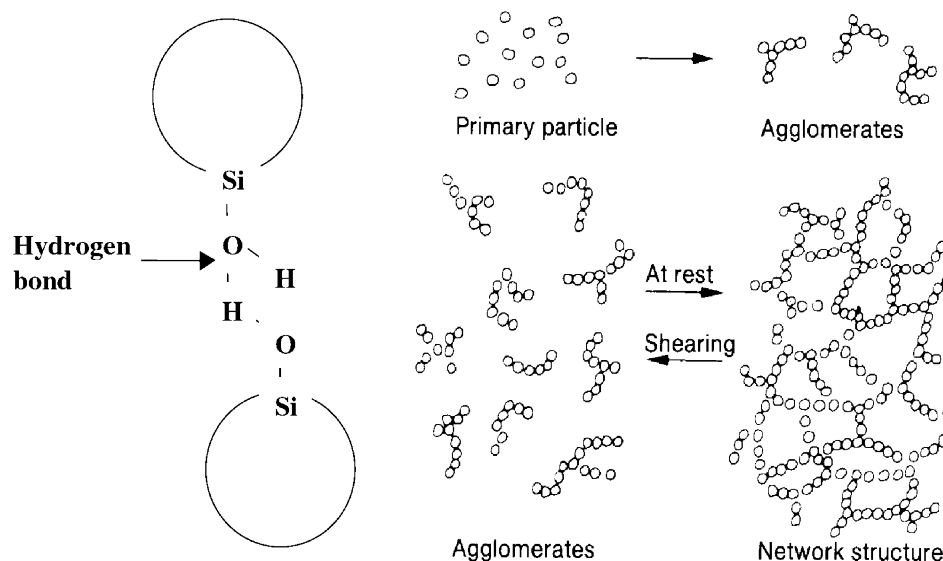


Fig. 2—Bond between molecules and gel formation.<sup>1</sup>

**Table 1—Chemical and physical properties of cement**

Constituent	Mass, %	Bogue composition	Mass, %
SiO <sub>2</sub>	21.1	C <sub>3</sub> S	60
Al <sub>2</sub> O <sub>3</sub>	4.4	C <sub>2</sub> S	15
Fe <sub>2</sub> O <sub>3</sub>	2.6	C <sub>3</sub> A	6
CaO	62.0	C <sub>4</sub> AF	8
MgO	2.8		
SO <sub>3</sub>	2.7		
K <sub>2</sub> O	0.7		
Na <sub>2</sub> O	0.25		
Na <sub>2</sub> O equivalent	0.7		
Free lime	0.5		
L.O.I.	3.0		
Surface blaine, m <sup>2</sup> /kg	345		

(w/c) of 0.40 and were tested for thixotropy, rheological properties, various stability indexes, heat flux, setting time, and compressive strength development.

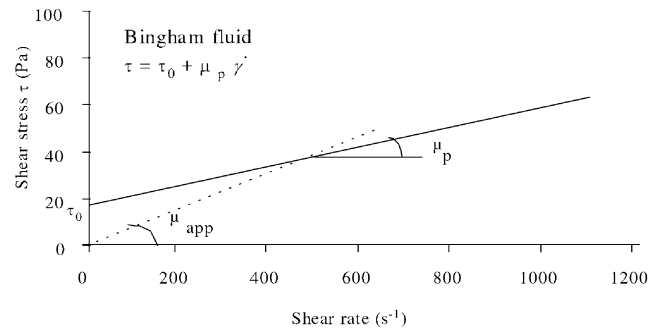
Phase II involved the optimization of flowable concrete containing PPC combined with powder hydropropyl methyl cellulose (HPMC). Six concretes of similar mixture proportioning and an initial slump of 200 ± 10 mm were investigated. The evaluated mixtures included a control concrete made without VEA, a concrete with a moderate dosage of PPC (0.5% by mass of water), two mixtures with low dosages of powdered HPMC (0.15% and 0.3% by mass of water), as well as two mixtures with 0.5% PPC and 0.15 and 0.3% HPMC. The concrete mixtures were tested for washout resistance, slump loss over 60 min, surface settlement, bleeding, setting time, and compressive strength.

**MATERIALS**

A Type 10 Canadian cement (CSA3-A5-M93) similar to ASTM Type I cement was used. Its chemical and physical characteristics are presented in Table 1. Crushed limestone aggregate with a 14 mm nominal size was used for the concrete mixtures evaluated in Phase II. The absorption of coarse aggregate totaled 0.4%. Riverbed siliceous sand with a 1.2% absorption, a fineness modulus of 2.5, and a specific gravity of 2.69 was used for the concrete mixtures. Both the sand and the coarse aggregate were well graded and conformed to the Canadian CSA A23.26.6 Standards.

In addition to the PPC, powdered HPMC and microbial polysaccharide welan gum were used for the VEA. A liquid-based cellulose VEA was also employed in the grout tested in Phase I. The water present in the liquid-based cellulose VEA is accounted for in the mixture proportioning. The powdered HPMC was also used in combination with the PPC thixotropic admixture in Phase II. Small dosages of tributyl phosphate were incorporated in mixtures containing HPMC to deaerate entrapped air.

A naphthalene-based HRWR (PNS) conforming to CSA3-A266.6-M85 was used. Its solid content and specific gravity were 42% and 1.21, respectively. This HRWR was used in mixtures containing welan gum and those made without VEA. A melamine-based HRWR (PMS) conforming to CSA3-A266.6-M85 was also used in mixtures incorporating PPC, as well as those with the liquid-based cellulose VEA and powdered HPMC. Such HRWR was employed because the PNS can exhibit some incompatibility with the HPMC and PPC that can lead to a sharper degree of fluidity loss. The solid content and specific gravity of the PMS are 40% and 1.20, respectively.



*Fig. 3—Relationship between shear stress and shear rate of Bingham fluid; plastic viscosity  $\mu_p$  corresponds to slope of linear regression, while apparent viscosity  $\mu_{app}$  is determined at any given shear rate.*

**TEST METHODS**

**Grout mixing and testing**

All grout mixtures were prepared in 4-L batches and mixed with a high-shear mixer operating at 2500 to 3000 rpm. The mixing sequence consisted of introducing water at 15 °C into the mixer along with the HRWR and VEA. The cement was added gradually over 60 s with the mixer running. The mixing continued for 120 s at 2500 to 3000 rpm.

A modified Marsh cone with a capacity of 1.2 L and an orifice diameter of 4.56 mm was used to assess the consistency. The efflux time corresponding to flow out of 700 mL of grout was noted. Rheological properties were determined using a coaxial cylinder viscometer with a 38-mm-high bob and a 1.17 mm gap between the bob and the rotor. The viscosity was determined at 11 rotational speeds varying between 1 and 600 rpm, corresponding to shear rate values of 1.7 and 1020 s<sup>-1</sup>. For each rotational speed, the grout was mixed for 20 s, and the angular deformation related to shear stress was noted. A linear regression was used to correlate the shear stress and shear rate values determined at the descending branch to calculate yield value and plastic viscosity, assuming the Bingham flow model for the fluid grout. As illustrated in Fig. 3, the Bingham model is expressed as  $\tau = \tau_0 + \mu_p \dot{\gamma}$  where  $\tau$ ,  $\tau_0$ ,  $\mu_p$ , and  $\dot{\gamma}$  correspond to shear stress, yield value, plastic viscosity, and shear rate, respectively.

The loss of fluidity was evaluated over 60 min following the initial contact of the cement with water. The shear history prior to determining the Marsh cone flow consistency after 30 and 60 min of age was as follows: the grout was placed in sealed containers and maintained at rest; and the grout was mixed by hand with a spatula for 5 s prior to conducting the test.

In the case of the coaxial viscometer, the grout remained covered in the recipient of the viscometer at rest between the 5- and 30-min and the 60-min test durations.

The coaxial viscometer was also used to assess the thixotropic behavior of the grout where variations of shear stresses over time were noted for mixtures subjected to a given rotational velocity. Such velocities were set at 3, 30, and 300 rpm corresponding to shear rates of 5.1, 51, and 510 s<sup>-1</sup>, respectively. The thixotropy was quantified by the difference between the maximum initial shear stress and shear stress at equilibrium determined during 5- to 9-min test durations. The differences in shear stresses were plotted against shear rates for grouts tested at different ages. The area between these curves and the horizontal shear rate axis offers a quantitative measurement of the energy necessary to break down

**Table 2—Test results of grouts investigated in Phase I**

Grout mixture	Welan gum + PNS	Liquid-based cellulose (HPMC) + PMS	PPC + PMS	PNS
w/c	0.40	0.40	0.40	0.40
HRWR, % C	1.6	1.2	1.5	0.5
VEA	0.0125% cement (0.031% water)	60 mL/100 kg cement	0.7% water	0
Temperature, °C	24.3	22.1	22.5	21.0
Specific gravity	1.99	1.94	1.94	1.91
Marsh cone flow at 700 mL, s	5 min	52	52	49
	30 min	65	94	115
	60 min	69	105	119
Yield value, Pa	5 min	0.08	1.007	1.71
	30 min	0.18	0.94	2.43
	60 min	0.62	1.07	1.85
Plastic viscosity, Pa.s	5 min	0.075	0.084	0.089
	30 min	0.073	0.097	0.091
	60 min	0.073	0.095	0.103
Forced bleeding, %	5 min	0.04	12	26
	60 min	0.03	12	22
Static bleeding, mL/cm <sup>2</sup>	0.08	1.0	0	—
Setting time, h	Initial	10.5	8.75	6.75
	Final	11.25	10.0	8.0
Compressive strength, MPa	1 day	18.5	15.2	20.8
	7 days	32.8	23	36.4
	28 days	44.3	33.2	54.4

the inter-particle bond in cement paste, hence reflecting the degree of thixotropy, as illustrated in Fig. 1.<sup>6</sup>

The stability of the fresh grout was evaluated by determining the degree of water retention in the mixture when it was subjected to a given pressure gradient. The resistance of the grout to pressure filtration or forced bleeding was measured using a filter at a pressure of 0.55 MPa.<sup>7</sup> The bleed water was collected over 10 min, and its volume is calculated as a fraction of the total water in the 200-mL grout sample.

The static bleeding was determined by observing the height of free water on top of a grout sample placed in a 250-mL graduated cylinder measuring 75 mm in diameter. The initial grout height was 100 mm. The cumulative height of the water was noted at 10-min intervals until the cessation of bleeding.

The setting time was measured using the Vicat needle test (ASTM C 953-87). An adiabatic calorimeter was used to evaluate the kinetics of cement hydration over 24 h. The determination of heat flux enables the evaluation of the differences in the kinetics of cement hydration during the stiffening and initial hardening periods. Compressive strength was evaluated using 50-mm mortar cubes. The mortar was prepared with the cement grout evaluated in this study that was mixed with standard sand (Ottawa sand, ASTM C 109) to reduce the risk of subsidence and microcracking in the neat cement paste samples. The sand-cement ratio was kept at 2.75 by mass. The cubes were demolded after one day and stored in lime-saturated water at  $19 \pm 1$  °C until the time of testing.

### Concrete mixing and testing

The majority of the concrete mixtures was prepared in batches of 100 L using an open-pan mixer. The mixing procedure consisted of homogenizing the sand and coarse aggregate with half of the mixing water for 30 s. The cement was then added, followed by the HRWR and the remaining water. The liquid-based VEA was introduced last and the concrete was

mixed for 3 min. After 3 min of rest, the concrete was remixed for 2 additional min. The ambient temperature during the mixing and testing of fresh concrete properties was maintained at  $21 \pm 3$  °C.

Following the end of mixing, the slump (ASTM C 143-90), unit weight, and air content were determined. The washout mass loss was tested in compliance with the CRD C 61 Standard.<sup>8</sup> The test consisted of placing approximately 2 kg of fresh concrete in a perforated basket and subjecting it to three free-fall drops in a 1.7 m-high water column. The surface settlement was evaluated by casting the concrete in a PVC column measuring 200 mm in diameter and 700 mm in height.<sup>9</sup> The concrete was cast in two lifts, each tamped 13 times using a 20 mm diameter tamping rod. The settlement was monitored until it reached steady-state conditions corresponding to the beginning of hardening.

The setting time was determined using the Proctor penetration test (ASTM C 403) on the mortar at  $21 \pm 2$  °C. Cylinders measuring 100 mm in diameter and 200 mm in height were prepared to evaluate compressive strength (ASTM C 39-94). They were demolded after one day and kept in lime-saturated water at  $21 \pm 2$  °C until the time of testing.

### RESULTS OF GROUT MIXTURES

Several mixtures were prepared to determine their HRWR demand for attaining the targeted Marsh cone flow time of  $50 \pm 2$  s. The following mixtures were selected:

- 0.7% PPC by mass of water + 1.5% PMS;
- 60 mL liquid-based cellulose product/100 kg cement + 1.2% of PMS;
- 0.0125% welan gum by mass of cement + 1.6% PNS; and
- 0.5% PNS without any VEA.

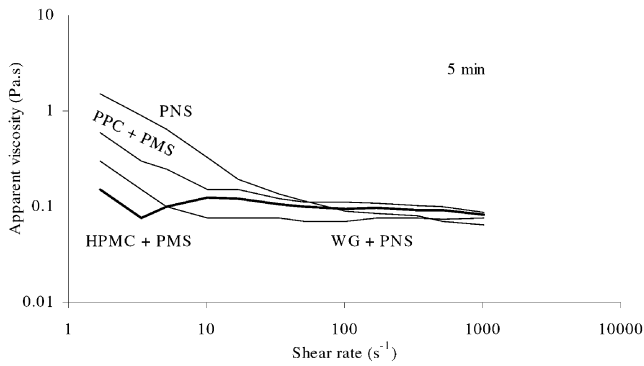


Fig. 4—Changes in apparent viscosity after 5 min of hydration.

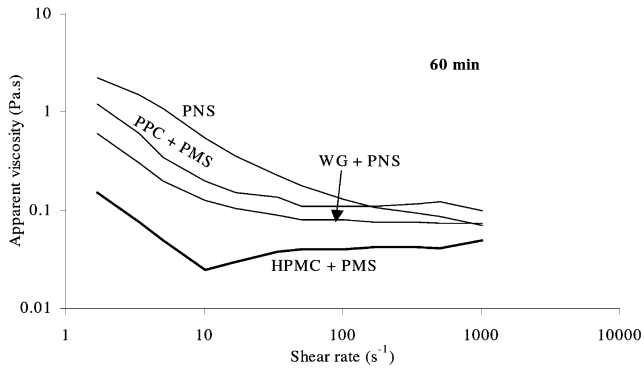


Fig. 5—Changes in apparent viscosity after 60 min of age.

### Marsh cone consistency and rheology

The four tested grouts had initial flow times of 49 to 52 s (Table 2). After 30 and 60 min, some differences in flow-time consistencies were noted. The grouts that exhibited limited loss in flow time were noted for the control PNS mixture and that made with welan gum and PNS. The mixture made with PPC and PMS exhibited the highest loss of fluidity, followed by that containing the liquid-based cellulose VEA and PMS grout.

As summarized in Table 2, the yield value of the grout containing welan gum was the lowest given the limited VEA dosage (0.0125% by mass of cement). Typical dosage rates of welan gum used to reduce bleeding in post-tensioning grouts can be twice as great. For the second mixture containing the liquid-based cellulose VEA, a low dosage of the polymer was also employed. This resulted in some sedimentation of solid particles during testing at high shear rates. The control grout made without any VEA and with PNS had the highest yield value of 3.0 Pa. The initial plastic viscosity and its variations were similar for all mixtures except for the PPC and PMS grout that exhibited a slightly greater rate of increase in the viscosity with time.

Figure 4 and 5 show the decrease in apparent viscosity with the increase in shear rate of grout mixtures tested after 5 and 60 min of age, respectively. Similar results were obtained at 30 min. The apparent viscosity was calculated as the ratio of shear stress to given shear rate as defined in Fig. 3. The resulting shear-thinning behavior was obtained mostly at shear rates lower than  $10 \text{ s}^{-1}$ ; the viscosity did not vary much at higher shear rates. As was the case with the yield value, the apparent viscosity of the PPC grout at low shear rates was higher than the other mixtures regardless of the test age. Such behavior was maintained at higher shear rates. The control PNS grout with the lowest HRWR demand of 0.5% PNS exhibited the

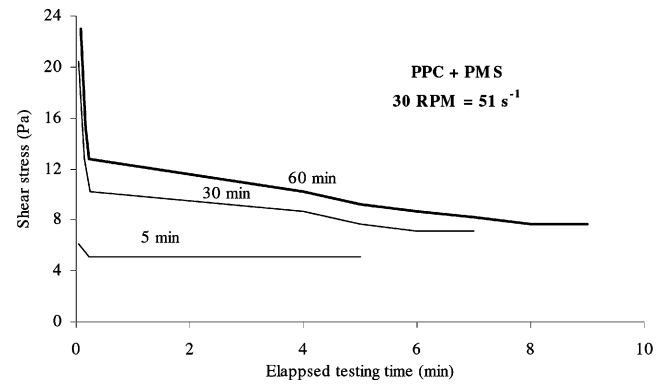


Fig. 6—Changes in shear stress for grout with PPC tested at 30 rpm.

highest apparent viscosity at low shear rates. This is in agreement with the high yield value of the control grout that had the shortest setting time among the four tested mixtures.

### Thixotropy

Figure 6 illustrates typical thixotropic behavior of the grout made with PPC (PPC and PMS). The mixture is shown to exhibit some fluidity recovery following a given shearing action at  $51 \text{ s}^{-1}$  (30 rpm). Compared with the initial testing at 5 min of age, initial shear stresses were considerably higher after 30 and 60 min. It should be emphasized that the shear recovery and thixotropic behavior tests were carried out on the same grout sample tested at 5, 30, and 60 min, with each test repeated at three shear rates each taking 5 to 9 min to ensure steady-state flow conditions. For each test age, especially those at 30 and 60 min, the shear stress of the PPC and PMS grout is shown to decrease considerably with the shearing duration, indicating a structural breakdown of the grout. The spread in shear stress between the initial value and that at equilibrium increased with the shear rate. According to Lapasin, Longo, and Rajgelj,<sup>6</sup> cement paste subjected to high dispersion by energetic agitation can exhibit the most rapid recovery after mixing and can exhibit antithixotropic behavior if the process of recovery takes place during the shearing action.

For the welan gum and PNS grout tested at  $510 \text{ s}^{-1}$ , the maximum change in shear stress did not vary considerably over the 7- to 9-min test period, which was observed again at 30 and 60 min of age. When tested at a lower shear rate of  $51 \text{ s}^{-1}$  (30 rpm), the grout had similar changes in shear stress with time for the three tests carried out at 5, 30, and 60 min. The shear stress remained basically unchanged over time, and the time of recovery was immediately attained, indicating a low degree of thixotropy.

In the case of the grout made with the liquid-based cellulose (HPMC and PMS), limited changes in shear stress were observed over time. At a  $510 \text{ s}^{-1}$  shear rate, the shear stress decreased over time following a sharp initial increase in shear stress during the first few seconds when tested at 30 and 60 min. At low shear rate of  $5.1 \text{ s}^{-1}$ , the HPMC and PMS mixture—as in the case of the PPC and PMS grout—exhibited limited changes in shear stress over the approximately 8-min test period at all ages.

It is important to note that both the WG and PNS and the HPMC and PMS mixtures exhibited some reduction of the initial shear stress when tested at 30 and 60 min compared with the tests at 5 min. This could be due to the fact that the grout did not recover enough from the initial shearing action over the approximately 7- to 10-min testing period at each

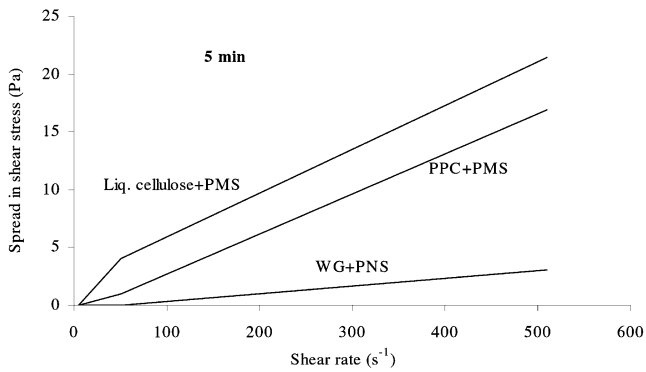


Fig. 7—Difference between maximum shear stress and stress at equilibrium of grouts tested at 5 min.

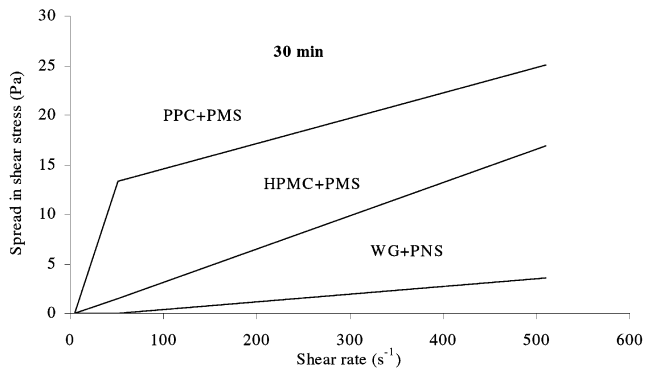


Fig. 8—Difference between maximum shear stress and stress at equilibrium of grouts tested at 30 min.

rotational velocity. Lack of a rest period can therefore prevent the restructuring of the grout from reestablishing its initial level of viscosity.

The difference between the maximum shear stress obtained during the 10-min test duration and the shear stress at equilibrium is used to quantify the thixotropy. Such spreads are plotted against shear rate in Fig. 7, 8, and 9 for the grouts tested after 5, 30, and 60 min of age, respectively. The area between these curves and the horizontal shear rate axis offers a quantitative measurement of the energy necessary to break down the interparticle bond in the cement paste. The power expended during the breakdown of the structure thus reflects the degree of thixotropy.<sup>6</sup> As shown in Fig. 10, the WG and PNS grout necessitated limited energy to break down the various chemical and physical bonds. Such values ranged from 500 to 700 Pa/s for the tests carried out at 5, 30, and 60 min. On the other hand, the HPMC and PMS grout required a high initial energy to break down the structure (approximately 6000 Pa/s at 5 min), which decreased to 4000 Pa/s when the test was carried out at 30 and 60 min of age. Again, this can be due to the lack of the rest period required for the restructuring of the grout between the initial and subsequent testing times. In the case of the PPC and PMS grout, the initial energy at 5 min was 4000 Pa/s, which increased to approximately 9000 and 8000 Pa/s after 30 and 60 min, respectively. These data clearly reflect the high capacity of the PPC to increase the thixotropic properties of the cement grout.

### Stability

As shown in Table 2, the welan gum and PNS grout had negligible forced bleeding values of 0.04 and 0.03% after 5 and 60 min, respectively, which reflects the ability of the

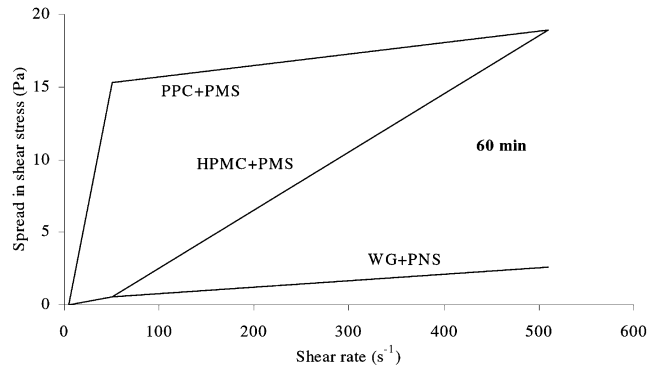


Fig. 9—Difference between maximum shear stress and stress at equilibrium of grouts tested at 60 min.

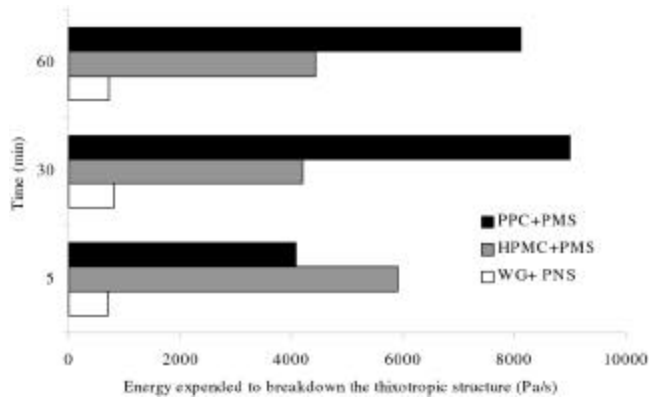


Fig. 10—Variation of energy necessary to break down thixotropic structure with time.

welan gum VEA to retain free water. The HPMC and PMS grout exhibited a high bleeding of 12% after 5 and 60 min. The PPC and PMS grout exhibited the highest bleeding of 26 and 22% after 5 and 60 min, respectively. Similar values were obtained with the non-VEA control grout (PNS).

Unlike forced bleeding, and in the absence of a pressure gradient, the PPC and PMS grout had no external static bleeding (or standing column bleeding) during the two-hour test period. The WG and PNS grout had a low static bleeding of 0.08 mL/cm<sup>2</sup>. The HPMC and PMS mixture, however, had a considerable bleed water of 1 mL/cm<sup>2</sup>, given its low VEA content.

### Setting time and heat flux

As given in Table 2, the control PNS grout made without any VEA and containing the lowest HRWR dosage had the shortest initial and final setting times of 5.9 and 7 h, respectively. Similar values were obtained with the PPC and PMS mixture incorporating the PPC (6.75 and 8 h, respectively). This was in spite of the relatively high concentration of the PMS (1.5%). The grout with the liquid-based cellulose admixture and PMS had an initial setting time of 8.75 h and a final setting time of 10 h. The WG and PNS grout exhibited higher initial and final setting times of 10.5 and 11.25 h, respectively, which was probably a consequence of the high concentration of HRWR at 1.6% by mass of cement.

The relative heat flux of the cement-based materials evaluated over 24 h is illustrated in Fig. 11. In general, the maximum rate of heat flux and its overall shape were similar to those of the control and other mixtures containing either the VEA or the thixotropic admixture. The shortest dormant period was obtained with the non-VEA grout containing 0.5% PNS; such a dosage of HRWR represents the lowest HRWR demand.

**Table 3—Composition and results of underwater concrete mixtures evaluated in Phase II**

Mixture	No VEA	0.5 PPC	0.15 HPMC	0.3 HPMC	0.5 PPC + 0.15 HPMC	0.5 PPC + 0.3 HPMC
Cement, kg/m <sup>3</sup>	421	418	420	425	415	413
w/c	0.41	0.41	0.41	0.41	0.41	0.41
Sand, kg/m <sup>3</sup>	742	736	744	754	736	732
5- to 14-mm aggregate, kg/m <sup>3</sup>	1095	1086	1100	1114	1086	1082
HRWR, L/m <sup>3</sup>	2.0	5.5	3.4	4.3	6.0	6.7
%C	0.23	0.63	0.4	0.5	0.70	0.78
PPC, % water	0	0.5	0	0	0.5	0.5
HPMC, % water	—	—	0.3	0.15	0.15	0.3
De-air, mL/m <sup>3</sup>	0	0	80	40	80	80
Slump, mm	10 min	225	230	230	220	210
	30 min	200	150	175	205	130
	45 min	—	—	145	195	85
	60 min	150	100	100	130	60
Air volume, %	1.5	1.7	1.6	1.8	2.0	2.4
Washout loss, %	8.5	6.9	10.1	9.0	6.6	3.3
Bleeding, 10 <sup>-3</sup> mL/cm <sup>2</sup>	32	46	0	0	0	0
Surface settlement, %	0.90	0.33	0.72	0.62	0.11	0.12
Initial set, h	6.17	8.67	5.58	5.08	6.00	6.33
Final set, h	8.07	11.33	6.67	6.25	7.16	7.75
Compressive strength, MPa	3 days	36.8	40.6	35.3	38.1	37.6
	28 days	47.6	43.1	47.6	49.3	51.5
	56 days	50.3	44.9	49.5	51.3	56.2

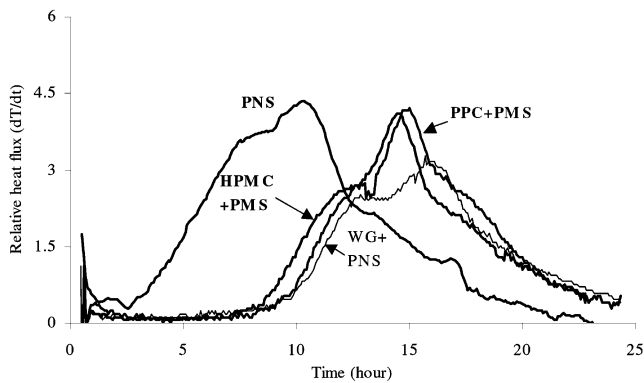


Fig. 11—Heat flux of tested grouts.

For the three mixtures with VEA or PPC that contained high dosages of HRWR, the lengths of the dormant periods were similar. The longest dormant period was obtained with the WG and PNS grout, and the shortest with the HPMC and PMS grout. The grout with PPC had an intermediate dormant period, which was close to that of the WG and PNS grout. The slight retardation in setting of the grout containing welan gum is, in part, due to the higher demand for HRWR and the nature of the HRWR, PNS compared with PMS used in the other two mixtures.

### Compressive strength

The mean compressive strength values of mortars made with grouts containing VEA and PPC are reported in Table 2. The PPC and PMS mixture had the highest 1-day compressive strength of approximately 21 MPa, compared with approximately 19 and 15 MPa for the WG and PNS and the

HPMC and PMS mixtures, respectively. After 7 days, this tendency was maintained with the highest strength observed being that of the PPC and PMS mortar (36 MPa), and the lowest being that of the cellulose and PMS mixture (23 MPa). After 28 days, the spread in compressive strength was even higher. The PPC and PMS mixture developed a strength of approximately 54 MPa, followed by the WG and PNS mortar (44 MPa), and the HPMC and PMS mixture (33 MPa).

### RESULTS OF CONCRETE MIXTURES

Six mixtures were prepared in Phase II to determine the HRWR demand required to secure an initial slump of 220 ± 10 mm. The slump loss, surface settlement, bleeding, setting time, and compressive strength development results are summarized in Table 3. The evaluated mixtures included: a control concrete made without any VEA, a concrete with a moderate dosage of PPC (0.5% by mass of water), two mixtures with low dosages of powdered HPMC (0.15 and 0.3%, by mass of water), as well as two mixtures with 0.5% PPC and 0.15 and 0.3% of the powdered HPMC. The 0.15 and 0.3% HPMC contents by mass of water correspond to 0.36 and 0.73% of cement mass that correspond to low and moderate dosages for the HPMC admixture when used in flowable underwater concrete to enhance stability.

### HRWR demand

The concrete mixtures had initial slump consistencies of 210 to 235 mm. The concrete without VEA had the lowest HRWR demand (2 L/m<sup>3</sup>) and exhibited the best slump retention. On the other hand, the two mixtures containing the PPC and HPMC admixtures had the highest HRWR demand (6 and 6.7 L/m<sup>3</sup>) and the lowest fluidity retention.



## Stability

The washout mass loss of the control (no-VEA) concrete was 8.5% after three standard drops in water content. The mixtures with HPMC also exhibited high washout losses of 9 and 10%. The concrete with 0.5% PPC (0.5 PPC) had a washout loss of 6.9% that was similar to that obtained with the 0.5 PPC and 0.15 HPMC concrete. With the greater HPMC dosage of 0.3%, however, the 0.5 PPC and 0.3 HPMC mixture exhibited a substantially lower washout loss of 3.3%. It is important to note that such low washout loss levels can be obtained for concrete of similar mixture proportioning and initial slump incorporating greater dosages of anti-washout admixture; for example, 900 mL cement/100 kg liquid-based cellulose admixture or 0.09% welan gum by mass of water.<sup>10</sup>

Both the no-VEA and 0.5 PPC mixtures exhibited relatively high bleeding values. The remaining concretes made with HPMC had no measurable external bleeding. The maximum surface settlement was quite high in the case of the control no-VEA concrete (0.9%) and the two HPMC mixtures (0.62 and 0.72%). Despite the high bleeding value, the 0.5 PPC concrete had a much lower settlement (0.33%) than the two HPMC mixtures. This value was even lower in the mixtures containing the PPC and HPMC admixtures combined (0.11 and 0.12%). The coupled effect of the VEA and thixotropic admixtures is shown to secure greater stability than the similar concrete incorporating either of the two admixtures.

## Setting and strength development

The concrete mixtures had initial and final setting times ranging approximately from 5 to 9 h, and from 6.25 to 11.5 h, respectively. The 0.5 PPC concrete had the highest setting time. All mixtures had similar compressive strengths at 3 days that ranged approximately from 37 to 41 MPa. The strengths at 28 days ranged approximately from 43 to 54 MPa, with the mixture made with a combination of PPC and HPMC exhibiting the highest strengths. These mixtures had also the highest strength values after 56 days of age. The 0.5 PPC concrete had the highest initial strength, but exhibited a lag of strength compared with the other mixtures.

## SUMMARY

This study demonstrates key differences between the effects of conventional VEA used to enhance stability and admixtures used to enhance thixotropic behavior of cement-based materials. Grout and concrete mixtures incorporating a PPC thixotropic admixture were shown to have a greater HRWR demand and a lower degree of fluidity retention than similar mixtures containing VEA such as welan gum and cellulose-based admixture. The use of PPC was shown to significantly

increase the thixotropic properties of cement grout. Grout made with welan gum had very a limited degrees of static and forced bleeding. The use of a low dosage of liquid-based cellulosic admixture was not efficient in eliminating static and forced bleeding. Such VEA admixture incorporated with a low PPC content, however, proved efficient in reducing time-dependent static bleeding, but not pressure filtration.

Using PPC was effective in reducing the risk of material separation in concrete during the plastic stage, and resulted in high resistance to bleeding and surface settlement. The incorporation of a moderate dosage of PPC was shown to enhance resistance to surface settlement and segregation. Again, both properties are time-dependent and are affected by the degree of thixotropy. The use of PPC alone did not have a significant effect on the instantaneous properties determined shortly after the end of mixing, such as washout.

Combinations of 0.5% PPC with powdered HPMC at low and medium contents of 0.15 and 0.3%, respectively, can result in highly flowable concrete with proper washout resistance and high resistance to bleeding and settlement without hindering setting time and strength development. Such concretes, however, exhibited sharper slump losses and greater HRWR demands than the remaining mixtures.

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