ISSN 0511-5728
The West Indian Journal of Engineering
Vol.37, No.2, January 2015, pp.68-73

Rheological Study of Cement Modified with a Lignin Based Admixture

Rean Maharaj[a], Lebert H. Grierson[b], Chris Maharaj[c, Ψ] and Vitra Ramjattan-Harry[d]

[a] University of Trinidad and Tobago, O'Meara Industrial Estate, O'Meara, Arima, Trinidad and Tobago, West Indies
E-mail: rean.maharaj@utt.edu.tt

[b] Department of Chemistry, University of the West Indies, St. Augustine, Trinidad and Tobago, West Indies;
E-mail: lebertgrierson@hotmail.com

[c] Department of Mechanical & Manufacturing Engineering, The University of the West Indies, St. Augustine, Trinidad and Tobago, West Indies; E-mail: chris.maharaj@sta.uwi.edu

[d] University of Trinidad and Tobago, Point Lisas Industrial Estate, Point Lisas, Trinidad and Tobago, West Indies
E-mail: vitra.harry@utt.edu.tt

Ψ - Corresponding Author

(Received 5 October 2014; Revised 31 December 2014; Accepted 30 January 2015)

Abstract: *Experiments involving the use of the dynamic shear rheology technique utilising a parallel plate configuration were conducted to investigate changes in the rheological properties of Trinidad Portland cement paste blended with Lignosulfonic acid, acetate sodium salt additive. The rheological properties of plastic viscosity (PV) and yield stress (YS) of the cement blend as defined by Bingham were calculated. Water/cement ratios of 0.40, 0.45 and 0.50 were used with a 0 - 0.50% additive at room temperature and the samples were tested at intervals of 10, 30, 60 and 90 minutes after mixing. The results showed maximum values of the PV between 0.05% and 0.10% admixture concentrations for the various water/cement ratios and time measurements. PV values were generally lower as water/cement ratios increased demonstrating improvements in the rheology. A PV value of 0.7 centipoise obtained with the control sample can be reproduced with the addition of approximately 0.05% admixture using 20% less water. Maximum values of YS generally occur between 0.05% and 0.10% admixture concentrations as a more compact, homogeneous paste system develops. Consistent with previous studies utilising this technique, YS data was generally sporadic. The ability to synthetically alter the rheological properties of Trinidad Portland cement adding a lignin based admixture can serve to optimise the strength, workability and shrinkage due to the reduced water-cement ratio.*

Keywords: *Portland cement; Rheology, Admixtures, Plastic Viscosity, Yield Stress, Lignin*

1. Introduction

In recent times there has been a marked increase in the use of mineral admixtures to improve the durability of concrete. Economic considerations mainly due to the necessity for lower cement requirement as well as environmental considerations have also contributed towards the increase in the usage of admixtures (Ferraris et al., 2001). Chemical admixtures are known to improve specific physical and mechanical properties of cement/concrete blends by modifying pore/void structures and enhancing interfacial cohesion between aggregate and cement paste and have been used to improve the quality of the concrete during mixing, transporting, placement and curing (Grierson et al., 2010; Faddi, 2011). However, the influence of admixtures on cement and concrete workability exhibits wide variability attributed to the origin of the raw material used in the cement manufacture, the place of manufacture, the cement composition and the type and concentration of the admixture (Collerpardi et al., 1983; Ben-Dor et al., 1985; Billingham and Coveney, 1993).

2. Literature Review

Concrete workability as defined by the American Concrete Institute (ACI) is the ease of placement of concrete, and practically is the ability of a fresh concrete mix to fill the form or mold without reducing the quality of the concrete. Workability is usually measured by the concrete slump test, following the ASTM C 143 or EN 12350-2 test standards. These tests for measuring workability have proven to require a large amount of material and labour and are very expensive (Ferraris et al., 2001). Researchers have successfully employed rheology tests based on the Bingham equation to describe the flow of concrete (Ferraris, 1999; Banfill, 2006; Mitsoulis, 2007; Mukhopadhyay and Jang, 2009). There are two basic parameters that characterise the rheology of the cement and concrete pastes: yield stress and plastic viscosity (Ferraris et al., 2001). As described by Ferraris et al. (2001), the yield stress is related to slump and the plastic viscosity is related to performance attributes such as stickiness, placeability, pumpability and finishability.

Lignosulfonates is a common plasticizer used in concrete manufacture where they reduce the amount of water required to make the concrete (giving stronger concrete) while still maintaining the ability of the concrete to flow and be pumped. Lignosulfonates are water-soluble anionic polyelectrolyte polymers obtained as a by-product in the production of wood pulp using sulfite pulping. The Howard process is a commonly used industrial method, in which 90–95% yields calcium lignosulfonates that are produced after precipitation with excess calcium hydroxide. They can also be separated from spent pulping liquids by Ultrafiltration and ion-exchange techniques. Lignosulfonates are also used as grinding aids in the cement mill and as a slurry deflocculant. The characteristic of lignosulfonates to reduce the viscosity of mineral slurries is utilised in oil drilling mud applications (Lebo et al., 2001).

In Trinidad and Tobago, research conducted by Grierson et al. (2004) investigated the influence of the admixture lignosulfonic acid, acetate sodium salt, on the chemical hydration of Trinidad Portland cement. They found that the lignin based admixture functioned as an inhibitor during hydration and as a dispersant, the ultimate effects manifested only during the latter stages of hydration, thereby improving the hardening properties of hydrated cements. Further work conducted by Grierson et al. (2010) measuring the influence of this admixture on the physical and mechanical properties of Trinidad Portland cement found that it altered the properties of apparent porosity (and water absorption), bulk density, compressive strength and setting times at different dosages and hydration times.

Although chemical admixtures are known to improve specific physical and mechanical properties of cement/concrete blends (Ferraris et al., 2001), the ability to formulate dosages of admixtures to improve the workability and ultimate performance qualities of Trinidad Portland cement has not been possible due to the unavailability of comprehensive research information on the low shear rate rheological (flow) properties of the cement-admixture blend. The effect of the admixture on the rheological properties of yield stress and plastic viscosity on Trinidad Portland cement remains unclear and additional information in the literature has proven limited. The ability to synthetically alter the flow properties of Trinidad Portland cement using a lignin based admixture can be very profitable and more sustainable approach since this base material is readily available as a by-product derived from plants.

Therefore, this paper seeks to investigate the rheological properties and in particular, the yield stress (YS) and plastic viscosity (PV) of Trinidad Portland cement blended with varying concentrations of lignosulfonic acid, acetate sodium salt, at different water/cement ratios.

3. Experimental procedures

3.1 The raw materials

The cement used was commercial grade ordinary Portland cement manufactured by Trinidad Cement Ltd. The lignosulfonic acid, acetate sodium salt, was purchased from Sigma-Aldrich Company, (catalogue number 370983-10G, lot number 00515CUV).

3.2 Sample Preparation

The initial pastes used to prepare samples for the rheological studies were of water/cement ratio of 0.40 by weight and were carried out at room temperature while the additive/cement percentage covered the range 0 - 0.50 %. The mass of the lignosulfonic acid, acetate sodium salt, admixture required was weighed using a Mettler Toledo AL204 analytical balance and dissolved in an amount of water appropriate to maintain the water/cement ratio constant at 0.40. The water containing the admixture and the cement were placed in a 25 ml beaker and mixed for two minutes using a digital IKA (Model RW20D) Overhead Stirrer**,** at approximately 450 rpm. This procedure was repeated for water cement ratios 0.45 and 0.50. The cement in the stated water/cement ratio is a combination of the mass of the cement and admixture. Table 1 shows the proportion of the constituents for the production of the different cement-additive blends for the different water/cement ratios.

Table 1. The proportion of the constituents for the production of the different cement-additive blends for the different water/cement ratios

% additive	**Mass of sample 20 g**					
	Water/Cement ratio 0.40		Water/Cement ratio 0.45		Water/Cement ratio 0.50	
	Mass of water (g)	Mass of additive (g)	Mass of water (g)	Mass of additive (g)	Mass of water (g)	Mass of additive (g)
0.00	8.00	0.00	9.00	0.00	10.00	0.00
0.05	8.00	0.01	9.00	0.01	10.00	0.01
0.10	8.00	0.02	9.00	0.02	10.00	0.02
0.30	8.00	0.06	9.00	0.06	10.00	0.06
0.50	8.00	0.10	9.00	0.10	10.00	0.10

3.3 Sample Characterisation

The rheological properties of plastic viscosity and yield stress of the cement blends as defined by Bingham were determined using an ATS RheoSystems Dynamic Shear Rheometer (Viscoanalyzer DSR) as outlined by Banfill (2006) and Mukhopadhyay and Jang (2009). The DSR test geometry used was the plate–plate configuration (diameters 25mm) with a 1 mm gap (sample thickness) and the measurements were conducted at 25°C. The cement paste to be analysed was placed on the bottom plate using a syringe. The gap was set to 1mm and the excess cement paste removed using a spatula. The shear rate was slowly increased from 0 to 200/s in ten steps (representing the up curve of the hysteresis loop) and then from 200 to 0/s in 10 steps (representing the down curve of the hysteresis loop) and the corresponding value of the shear stress recorded. The recorded value for each step in the up and down curves represented an average of 5 values measured by the instrument. The various blends containing 0%, 0.05%, 0.10%, 0.30% and 0.50% of the admixture by weight at water/cement ratios 0.40, 0.45 and 0.50 (a total of 15 different blends) were subjected to this analysis. Each of these blends was tested after intervals of 10, 30, 60 and 90 minutes after mixing.

The results obtained were analysed using the Viscoanalyzer software. Consistent with the methodology outlined by Banfill (2006) and Mukhopadhyay and Jang (2009), the values of the rheological parameters associated with the plastic viscosity and yield stress for each sample were determined from the plot of shear rate versus shear stress whereby the plastic viscosity was calculated from the slope of the linear region of the down curve (decreasing shear rate) and the yield stress was calculated from the intercept of the down curve and the y-axis.

4. Results and Discussion

Figure 1 shows the hysteresis loop for the blend at 0.40 water cement (w/c) ratio containing 0.10% admixture 10 minutes after mixing and the curve was typical of those obtained for all the cement-lignosulfonic acid, acetate sodium salt, admixture blends analysed in this study. This blend was randomly chosen to highlight consistency with previous work conducted by Banfill (2006) and Mukhopadhyay and Jang (2009).

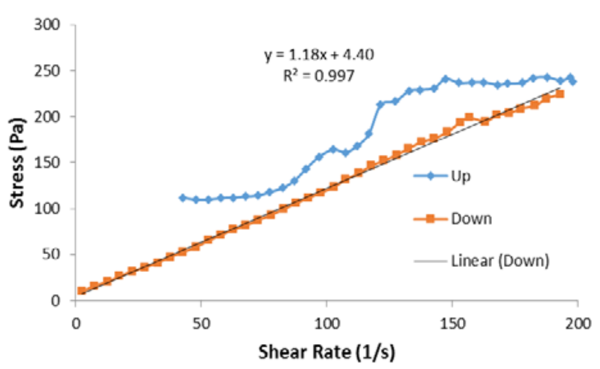

Figure 1. Graph shows the typical up and down curves for the sample at 0.4 w/c ratio containing 0.1% admixture after 10 minute

As seen in this example and from the equation of the linearized down line of the hysteresis loop (y = 1.18x + 4.40), the intercept of the down curve with the y-axis was 4.40 Pa and represents the yield stress (YS) of the blend whereas the gradient of the line was calculated to be 1.18 centipoise and represents the plastic viscosity (PV) of the blend.

The rheological parameter of PV as a function of admixture concentration for water/cement ratios 0.40, 0.45 and 0.50 for a time of 10 minutes after mixing is shown in Figure 2.

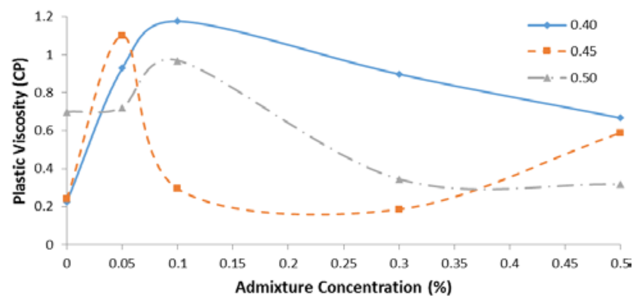

Figure 2. Plastic Viscosity vs. Admixture Concentration for various water/cement ratios after a mixing time of 10 minutes

The results demonstrate that after 10 minutes a maximum value of the PV was observed between 0.05% and 0.10% admixture concentrations. This indicates that the cement pastes containing these levels of admixtures demonstrate a relatively higher resistance to flow as it is relatively viscous due to the existence of greater amounts of colloidal solids (Alp et al., 1986). This observation correlates with results from a previous study conducted by Grierson et al. (2010) as they observed that the apparent porosity and the related parameter of water absorption of Trinidad Portland cement containing lignosulfonic acid, acetate sodium salt, at various aging times were generally lower for blends containing 0.05% plasticiser concentration. Grierson et al. (2010) associated these observed reductions at the 0.05% level of admixture with an increase in the inter-particle attraction between the cement particles, thus increasing agglomeration and reducing dispersion or deflocculation giving rise to a more homogeneous, compact paste system of lower porosity. However, at concentrations > 0.10%, they found that the lignin based surfactant sufficiently lowers the surface energy of the water, and thus the surface tension, allowing air entrainment to occur, resulting in higher porosity values.

The observations represented in Figure 2 also show that PV values were generally lower as water/cement ratios increased. Previous work conducted by Ferraris et al. (2001), obtained similar trends when investigating the influence of different water/cement ratios on the rheological properties of cement blends containing ultrafine fly ash. The purpose of their study was primarily to determine the level of water reduction accomplished by using the ultrafine fly ash admixture while maintaining the same YS and/or PV. In other words, the objective was to quantify the reduction of the water requirement due to the addition of ultrafine flyash or in our case lignosulfonic acid, acetate sodium salt, to the cement paste while maintaining the same YS and PV as the control. As can be seen from Figure 2, a PV value of 0.7 centipoise obtained with the control sample (no admixture added) at a water cement ratio of 0.50 can be obtained with the addition of approximately 0.05% lignosulfonic acid, acetate sodium salt, admixture with a 20% reduction in water requirement (water/cement ratio 0.4). This specific observation demonstrates a distinct advantage (reduction in water requirement) obtained in the rheological properties of the Trinidad cement paste blended with the lignin based additive and offered supporting evidence for previous work documented by Lebo et al., (2001).

The variation of PV with time after mixing for the different additive concentrations at a water/cement ratio of 0.50 is shown in Figure 3. What is most evident from the relationships obtained is that the PV value was highest for the paste containing 0.10% admixture for all the setting times measured. The blend containing 0.05% additive demonstrated a marginal increase in the PV compared to the control sample. As previously explained, this occurrence can be attributed to an increase in the inter-particle attraction and agglomeration thus reducing dispersion or deflocculation which gives rise to a more homogeneous, compact paste system of lower porosity and higher PV.

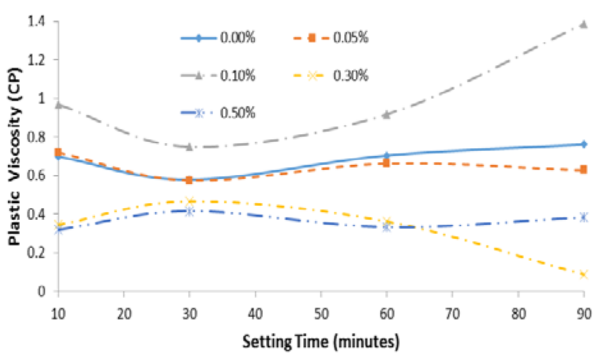

Figure 3. Plastic Viscosity vs. Time for the various Admixture Concentration at a water/cement ratios of 0.5

The unique rheological behaviour of the blends containing 0.05% and 0.10% additive was further exemplified in Figure 3 as these two blends demonstrated an initial decrease in their PV after 30 minutes after which the values gradually rise as the cement hydration processes continue and the pastes harden. The pastes containing 0.30% and 0.50% showed an opposite trend as the PV of the pastes maximised after 30 minutes. Although the PV of the paste containing 0.50% admixture subsequently increased after 90 minutes, the paste containing 0.30% admixture demonstrated a continued downward trend in the value of PV. The unique behaviour of the cement paste containing 0.30% admixture was previously observed by Grierson et al. (2010) where attempted measurements of physical parameters of porosity and bulk density at higher concentrations (>0.1%) of lignosulfonic acid, sodium salt, acetate in Trinidad Portland cement were not possible even after 2 days as the samples were too liquefied in nature.

As explained by Grierson et al. (2010), cement pastes containing high levels of this admixture (>0.1%) result in significant retardation of the hydration process of the cement particles which results in a highly dispersed, low viscosity substance. Studies conducted by Maximilien et al., (1997) and Grierson et al. (2004) associated changes in the hydration times with Ca^{2+} ion release. Grierson et al. (2004) found that the magnitude of the conductivity change of cement pastes containing 0% and 0.05% plasticiser was similar however the change was greater for the sample with 0.50% plasticizer. They suggested that while low concentrations of the plasticiser have little or no control over the release Ca^{2+} ions into the solution, blends containing 0.50% admixture or more act to inhibit Ca^{2+} release. Their observations showed that there is competition between the principal hydration reaction which causes the paste to harden and a plasticiser-induced inhibition of Ca^{2+} release, with the inhibition process dominating at 0.5% plasticiser concentration. At these high admixture levels, poisoning of the process of crystalline ettringite formation probably occurs which reduces initial C_3S hydration resulting in the highly dispersed and liquefied sample with a low PV as observed in this study.

Figure 4 shows the variation of Yield Stress (YS) as a function of Admixture concentration for water/cement ratios 0.40, 0.45 and 0.50 for times after mixing of 10 minutes. The maximum value of YS occurred at 0.05% concentration.

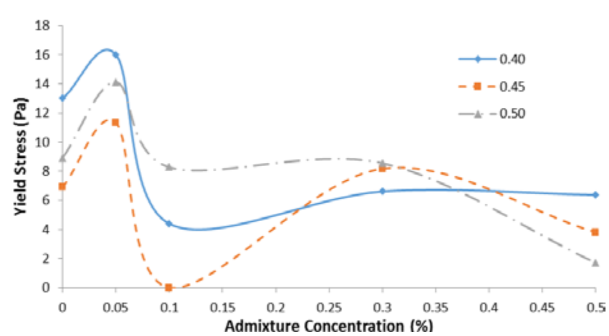

Figure 4. Yield Stress vs. Admixture Concentration for various water/cement ratios after a mixing time of 10 minutes

Figure 5 also shows the variation of Yield Stress (YS) as a function of Admixture concentration but for times after mixing of 30 minutes. The maximum value of YS occurred at 0.10% concentration. The maximum values of YS occurred within the concentration range of

0.05% to 0.10% for times after mixing of 60 and 90 minutes as well.

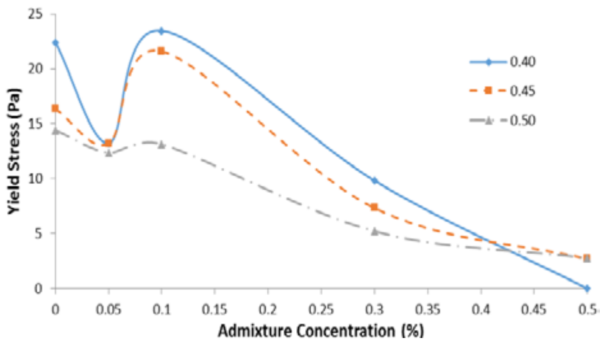

Figure 5. Yield Stress vs. Admixture Concentration for various water/cement ratios after a mixing time of 30 minutes

As explained by Grierson et al. (2010), yield stress is associated with slump and again the higher values observed between 0.05% and 0.10% can be associated with a reduction in the inter-particle attraction, and agglomeration of the cement particles and effecting dispersion or deflocculation. At these low concentrations of admixture, a more compact, homogeneous paste system with higher slump develops. It must be noted however that presentation of additional Yield Stress data proved difficult as these values were generally sporadic. The sporadic nature of the calculated YS data is not unique to this study and has also been reported by other researchers (Nedhi and Rahman, 2004), who associated errors in reliability when estimating yield stress values.

5. Conclusions

The addition of lignosulfonic acid, acetate sodium salt, to Trinidad Portland cement resulted in changes in the rheological properties of the blends as demonstrated by changes of both the PV and YS of the modified pastes. The results showed the following:

1) Maximum values of the PV were observed between 0.05 and 0.10% admixture concentrations for the various water/cement ratios and time measurements.
2) PV values were generally lower as water/cement ratios increased demonstrating improvements of the Trinidad cement paste blended with the additive. Addition of lignosulfonic acid, acetate sodium salt, can be used to obtain the same yield stress and PV as the control using significantly less water.
3) Maximum values of YS (directly associated with slump) also occurred between 0.05% and 0.10% addition of lignosulfonic acid, acetate sodium salt, for all water/cement ratios as a more compact, homogeneous paste system develops. Yield Stress data were generally sporadic associated with the reliability of estimating yield stress values.

Water-cement ratios beyond a minimum, generally 0.4, are required for suitable workability. However high water-cement ratios cause decrease in compressive strength and increase in shrinkage of concrete during curing and hence increased cracking. Therefore a compromise between strength, workability and shrinkage is necessary. Organic plasticisers allow better maintenance of workability of cement pastes at lower water-cement ratios with their expected improved hydrated cement properties. There is a drive to develop new improved plasticisers/superplasticisers with even lower workable water-cement ratios, especially those based on quasi-natural materials such as lignosulphonate (a derivative of wood pulp). The workability, i.e. plastic viscosity (PV) and yield stress (YS), results shown for (0.05 – 0.50%) lignosulphonate, sodium salt, acetate cement admixture compositions in this work (and from our previous work) make it a good candidate plasticiser for commercial use in the cement and concrete industry.

Acknowledgements:

The authors acknowledge research students Mr. Vivek Rampersad and Ms. Cheryon Morin of the University of the West Indies who assisted with the rheology experiments.

References:

Alp, E., Chilingarian, G.V., Caenn,R., Mouhammed Al-Salem, Uslu, S., Gonzales, S., Dorovi, R.J., Mathur, R.M., and Yen, T.F. (1986), "Drilling Fluid Evaluation Using Yield Point-Plastic Viscosity Correlation", *Energy Sources*, Vol. 8 No. 2-3, pp. 233-244

Banfill, P.F.G. (2006), "Rheology of fresh cement and concrete", *Rheology reviews*, pp. 61-130

Ben-Dor, L., Wirguin H. C., and Diab, H. (1985), "The effect of ionic polymers on the hydration of C_3S", *Cement and Concrete Research*, Vol.15, pp.681-686

Billingham, J. and Coveney, P.V. (1993), "Simple chemical clock reactions: Application to cement hydration", *Journal of the Chemical Society, Faraday Transactions*, Vol.89, pp.3021-3028.

Collepardi, M., Monosi, S., Moricini, G. and Pauri, M. (1983), "Influence of lignosulphonate, glucose and gluconate on the C_3A hydration", *Cement and Concrete Research*, Vol.13, pp.568-574.

Faddi, Norbert (2011), *Concrete Quality Improvement*, VIA University College, p.1-50.

Ferraris, C.F. (1999), "Measurement of the rheological properties of cement paste: A new approach", RILEM International Symposium on The Role of Admixtures in High Performance Concrete, 21st-26th March, Monterrey pp.333-342.

Ferraris, C.F., Obla, K.H. and Hill, R. (2001). "The influence of mineral admixtures on the rheology of cement paste and cement", *Cement and Concrete Research*, Vol.31, No.2, pp.245-255.

Grierson, L.H., Knight, J.C. and Maharaj, R. (2004), "The role of calcium ions and lignosulphonate plasticiser in the hydration of cement", *Cement and Concrete Research*, Vol.35, pp.631-636.

Grierson, L., Maharaj, R. and Knight, J.C. (2010), "The effect of lignosulphonic acid, sodium salt, acetate on the physical and mechanical properties of Trinidad Portland cement", *International Journal of Material Science*, Vol.5, No.1, pp.75-82.

Lebo, Stuart E. Jr.; Gargulak, Jerry D. and McNally, Timothy J.

(2001), "Lignin", In: *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons, Inc.

Maximilien, S., Pera, J. and Chabannet, M. (1997), "Study of the reactivity of clinker by means of the conductometric test", *Cement and Concrete Research*, Vol.27, No.1, pp.63-73.

Mathur, R.M. and Yen, T.F. (1986), "Drilling fluid evaluation using yield point-plastic viscosity correlation", *Energy Sources*, Vol.8, No.2-3, pp. 233-244

Mitsoulis, Evan (2007), "Flows of viscoplastic materials: Models and Computations", *Rheology Reviews*, pp.135-178.

Mukhopadhyay, A.K. and Jang, S. (2009), *Using Cement Paste Rheology to Predict Concrete Mix Design Problems*, Accessed from http://tti.tamu.edu/documents/0-5820.pdf

Nehdi, M. and Rahman, M.-A. (2004), *Effect of Geometry and Surface Friction of Test Accessory on Oscillatory Rheological Properties of Cement Pastes*, ACI Materials, No. 101-M47.

Authors' Biographical Notes:

Rean Maharaj *is holder of a Bachelors (B.Sc.) Degree in Chemistry, specialising in Analytical Chemistry at The University of the West Indies (UWI), St. Augustine, a Masters of Philosophy (M.Phil.) degree in the field of Applied Physical Chemistry (UWI) and a PhD. Degree in Process and Utilities Engineering from The University of Trinidad and Tobago. Dr. Maharaj spent several years as a Forensic Analyst at the Trinidad and Tobago Forensic Science. He was extensively trained in Forensic Chemistry under a United Nations Fellowship drug training programme and by the US Drug Enforcement Agency (DEA). He is currently Assistant Professor in Process Engineering of The University of Trinidad and Tobago (UTT). His research interests are mainly based in the applied chemistry/materials science area including cement and asphalt technology.*

Lebert H. Grierson, *former Head of Chemistry Department, is a Lecturer in Physical Chemistry in the Chemistry Department of The University of the West Indies. He holds BSc and PhD from The University of London. He did postdoctoral work at The Chemistry Department, Rijkuniversitat Groningen, The Netherlands and then at Max Planck Institute for Strahlenchemie (Radiation Chemistry) in Muelheim a.d. Ruhr, Germany between 1988-1991. His present research interest focuses on applied physical chemistry including topic such as waste polymer cracking using fluidised-bed technology, asphalt and cement research and application of microcalorimetry techniques to biological systems.*

Chris Maharaj *is a Lecturer in the Mechanical and Manufacturing Engineering Department of The University of the West Indies (UWI). He holds BSc and MSc qualifications in Mechanical Engineering and Engineering Management respectively from UWI. He started his career as a Mechanical Engineer in Condition Monitoring and Inspection and worked in the industry for five years. He later went on to pursue his PhD at Imperial College London in Mechanical Engineering. His present teaching and research interests are in alternative use of waste materials, mechanical design optimisation, failure analysis, component life assessment, asset management, and innovation management.*

Vitra Ramjattan-Harry *is a Laboratory Technician in the Process Engineering Department at The University of Trinidad and Tobago (UTT). She has a B. Eng. in Process and Utilities Engineering and has work experience in both the Food and Chemical Industries where she was involved with product and process optimisation, quality control and ISO certification. At UTT, she assists research, postgraduates and final year students by providing technical support for the analytical equipment in the Material Characterisation laboratory.*

■