

## **Effect of Modified Lignosulphonate Superplasticizer on Workability Retention and Initial Setting of Cement Pastes**

**Min-Hong Zhang<sup>1</sup> and Kåre Reknes<sup>2</sup>**

<sup>1</sup> *Department of Civil Engineering, National University of Singapore, 1 Engineering Drive 2, Singapore. E-mail: <cvezmh@nus.edu.sg>.*

<sup>2</sup> *Borregaard Ind. Ltd., Department: LignoTech, Hjalmar Wessels vei 10, P.O.Box 162, N-1701 Sarpsborg, Norway. Email: <kare.reknes@borregaard.com>.*

### **ABSTRACT**

This paper presents an experimental study on the effect of a newly developed modified lignosulphonate (PLS) superplasticizer on the workability retention and initial setting time of cement pastes in comparison to those of polycarboxylate (PCE) and naphthalene (SNF) superplasticizers. The workability retention was monitored by yield stress and effective viscosity of the pastes. The initial setting was determined by penetration depth in cement pastes. Different dosages of the superplasticizers were used to obtain cement pastes with yield stress < 6 Pa at 30 minutes at given water-to-cement ratios of 0.26 and 0.32. The results indicate that the paste with the PLS admixture had longer workable time and initial setting time than that with the PCE and SNF admixtures. Although the longer workable time is beneficial for hot weather concreting, the longer initial setting time of such material has to be taken into consideration where early strength development is essential.

### **INTRODUCTION**

Properties of hardened cement paste and concrete are affected by their flow behavior which is controlled primarily by the dispersing of cement in mixing water and concrete mixture design. Superplasticizers have been used extensively to disperse the cement and to improve the workability of concrete in practice. In hot weather conditions, superplasticizers with retarding effects are commonly used to reduce the rate of cement hydration and to extend workable time at jobsites to reduce pumping problems and to prevent cold joints. Thus, the selection of adequate chemical admixtures and to evaluate their effect on early age properties such as workability retention and initial setting time are of significant importance. These properties may consequently influence the behavior of hardened cement pastes and concretes.

Among commonly used superplasticizers such as polycarboxylate, naphthalene, melamine, and modified lignosulphonate admixtures, only modified lignosulphonate admixtures are produced and derived from natural materials. Lignin is produced in the nature and is after cellulose the second most abundant natural polymer. There is typically 40-45% cellulose and 30-35% lignin in wood. Lignosulfonate is produced from lignin through a sulfonation process that makes the lignin polymer water soluble. In nature, photosynthesis uses sunlight to convert CO<sub>2</sub> to sugars and oxygen. The sugars are converted into cellulose and the monomers that are used for making lignin. The lignin is made through complex chemical processes from

its monomers: p-coumaryl alcohol, coniferyl alcohol and sinaphyl alcohol. The ratio between the different monomers is different between softwood, hardwood and annual plants. Approximately 1.5 kg of CO<sub>2</sub> is removed from the atmosphere for every kg of lignin produced by the photosynthesis. During the pulping process and chemical modifications of the lignin into different lignosulfonate products, some CO<sub>2</sub> is released. However, this CO<sub>2</sub> release is small and the result is a net removal of carbon from the carbon cycle. The carbon contained in the lignosulfonate product is embedded in concrete when lignosulphonate is used as an admixture. It is not released again and the carbon is thus removed from the carbon cycle.

Lignosulphonates (LS) have been widely used in concrete as regular water reducing admixtures for many years due to their relatively low prices and good cost/performance ratio. Significant advances have been made in the production of LS based admixtures. With the development of a new modified LS superplasticizer (PLS), it has been reported that it is possible to produce self-compacting concrete [Reknes and Peterson 2003]. However, there is not much information available on the effect of the PLS admixture on workability retention and initial setting time of cement pastes.

Earlier research [Sun et al. 2009] on comparison of the PLS admixture with naphthalene (SNF) and polycarboxylate (PCE) based superplasticizers shows that the adsorption of the superplasticisers was strongly dependent on the type of admixture used in cement pastes. The superplasticisers delayed cement hydration at early age, but did not have significant effect on the cement hydration beyond 7 days. The retardation of the cement pastes with given workability are in an order of SNF < PCE < PLS.

This paper presents an experimental study on the effect of the newly developed modified lignosulphonate superplasticizer (PLS) on workability retention and initial setting time of cement paste in comparison to those with SNF and PCE superplasticizers. The workability retention was evaluated based on the change of yield stress and effective viscosity with time. The initial setting time was evaluated based on penetration depth in cement pastes. Proportion of mixtures with various superplasticizers was designed so that the yield stress of the cement pastes was less than 6 Pa at 30 minutes. The results will provide basic information for design concrete mixtures with different superplasticizers.

## **DETERMINING WORKABILITY RETENTION AND INITIAL SETTING**

### **Change of Rheological Parameters with Time and Workability Retention**

Workability change with time is of significance in practice for transportation and casting of concrete before the initial set. The workability retention may be evaluated by the change in rheological parameters with time. With continued cement hydration, cement paste and concrete lose workability, and eventually set.

The flow of cement pastes has been reported to fit several different mathematical forms [Banfill 2003] e.g. Bingham  $\tau = \tau_o + \eta\dot{\gamma}$  and Herschel-Bulkley  $\tau = \tau_o + K\dot{\gamma}^n$  models, where  $\tau$  is shear stress applied to material in Pa,  $\tau_o$  is yield stress in Pa, and  $\dot{\gamma}$  is shear rate in s<sup>-1</sup>. In Bingham model,  $\eta$  is plastic viscosity in Pa's and is assumed to be constant. In Herschel-Bulkley model, K is the consistency index and n is the power-law index. The Herschel-Bulkley model takes into account changes in the effective viscosity with shear rate by assuming the power-law expression,  $\eta = K\dot{\gamma}^{n-1}$  [Burgos and Alexandrou 1999].

Depending on the value of “n”, the material flows as a shear thinning fluid ( $n < 1$ ) or as a shear thickening fluid ( $n > 1$ ).

The yield stress is the minimum shear stress that must be exceeded in order for the material to flow. Once the flow has started, the effective viscosity determines flow rate of the cement pastes. Lower yield stress and plastic (or effective) viscosity usually correspond to better flowability and workability.

### **Initial Setting**

Setting is a term used to describe the stiffening of the cement paste, mortar, or concrete. In principle, the setting of cement is a process in which isolated or weakly bound particles are connected by the formation of hydration products so that solid paths are formed in the hardening pastes [D’Angelo et al. 1995; Jiang et al. 1995; Bentz 2007; Garcia et al. 2008]. The setting of cement pastes, therefore, will depend on factors that affect the connectivity level between particles such as w/c [Bentz 2007; Garcia et al. 2008] and degree of cement hydration.

In practice, the initial set indicates the loss of workability significantly and the beginning of stiffening of the paste or concrete. Initial setting of cement may be determined by ASTM methods C 191 based on principle of penetration depth. In this test method, normal consistency of the paste is required. According to ASTM C 191, the initial setting of a cement paste occurs when the Vicat needle penetrates 25 mm into the cement paste.

## **EXPERIMENTAL DETAILS**

### **Materials Used**

Portland cement of ASTM Type I (Table 1) was used in the study, and deionized water was used for cement pastes. Modified lignosulphonate (PLS)<sup>1</sup>, naphthalene (SNF)<sup>2</sup>, and polycarboxylate (PCE)<sup>3</sup> based superplasticizers were included in this study. Their characteristics are summarized in Table 2. Approximately 0.5% tributylphosphate by mass of dry admixture was added to the solutions of all three admixtures to control the air that may be entrained.

### **Proportion of Cement Paste Mixtures**

Proportion of mixtures with various superplasticizers was designed so that the yield stress of the cement pastes was less than 6 Pa at 30 minutes. The mix proportions of the cement pastes used in this research are shown in Table 3. The w/c ratios of the cement pastes were 0.26 and 0.32.

### **Test Methods**

#### ***Determine rheological parameters of cement pastes***

Rheological parameters were determined at various intervals from the time water and admixture was in contact with the cement until the yield stress of the cement pastes increased sharply compared with that at initial stage.

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<sup>1</sup> Modified lignosulphonate (Solus 5), by Borregaard Lignotech, Norway.

<sup>2</sup> Naphthalene formaldehyde condensate (Tamol NH 8807 L), Rohm and Haas, UK.

<sup>3</sup> Polycarboxylate (Sokalan HP 80), by BASF Corporation, Germany.

**Table 1 - Physical Properties and Composition of Cement Used**

Physical Properties	Initial Setting Time, min	145
	Final Setting Time, min	210
	Blaine Fineness, m <sup>2</sup> /kg	391
Chemical Composition, %	Calcium Oxide, CaO	65.0
	Silica, SiO <sub>2</sub>	20.3
	Aluminum Oxide, Al <sub>2</sub> O <sub>3</sub>	4.7
	Iron Oxide, Fe <sub>2</sub> O <sub>3</sub>	3.2
	Magnesia, MgO	0.9
	Sodium Oxide, Na <sub>2</sub> O	0.2
	Potassium Oxide, K <sub>2</sub> O	0.5
	Total Alkalinity as Na <sub>2</sub> O+0.658K <sub>2</sub> O	0.53
	Sulphuric Anhydride as SO <sub>3</sub>	2.4
	Loss on Ignition (LOI)	1.9
Mineral Composition According to Bogue Calculation, %	Tricalcium Silicate, C <sub>3</sub> S	67
	Dicalcium Silicate, C <sub>2</sub> S	8
	Tricalcium Aluminate, C <sub>3</sub> A	7
	Tetracalcium Aluminoferrite, C <sub>4</sub> AF	10

**Table 2 - Characteristics of Admixtures Used**

Type	Notation	ASTM Type	Reducing substances, %	Soluble SO <sub>4</sub> , % of dry admixture
Polycarboxylate	PCE	F	n.m.	n.m.
Naphthalene	SNF	F	n.m.	n.m.
Modified Lignosulphonate	PLS	G/F	0.5	0.2

n.m.: not measured

**Table 3 - Mix Proportion of Cement Pastes**

Mix	Water/Cement	Superplasticizer type	Superplasticizer dosage, % sbmc <sup>(a)</sup>
1		No admixture	-
2	0.26	PCE	0.13
3		SNF	0.39
4		PLS	0.35
5		No admixture	-
6	0.32	PCE	0.10
7		SNF	0.30
8		PLS	0.28

<sup>(a)</sup> sbmc: solid by mass of cement, %

The admixture was added into mixing water and then mixed with the cement in a Hobart mixer for about 4 minutes. Before each test, the paste was remixed in the mixer for about 10 seconds.

A Hakka RV1 rheometer with coaxial cylinder configuration was used to determine the rheological parameters of the cement pastes. The torque resulting from the material resistance was measured at the inner rotating cylinder, which had a length of 55 mm and a diameter of 38 mm. Gap between the inner and outer cylinders was 2.7 mm. The surfaces of the inner and outer cylinders were serrated so that the slippage between the cement paste samples and the surfaces of the cylinders was minimized. The shear rate first increased from 0.5 to 50 s<sup>-1</sup>, and then decreased to 0.5 s<sup>-1</sup>. The down curve (from 50 to 5 s<sup>-1</sup>) was used to calculate the yield stress of the cement paste based on Herschel-Bulkley model. Due to the shape of the curves, using Bingham model fitting resulted in negative yield stresses as observed by de Larrard et al. [1998] as well. The data, therefore, were fitted by Herschel-Bulkley model to determine the yield stress  $\tau_0$ , consistency index K, and power law index n. From the parameters of “K” and “n” in Herschel-Bulkley model, effective viscosity of the cement pastes was calculated at  $\dot{\gamma} = 25 \text{ s}^{-1}$ .

#### ***Determine initial setting time of cement pastes by penetration depth method***

The initial setting time of the cement pastes was determined according to ASTM C 191 Method B with modification using an automatic Vicat apparatus. ASTM Method specifies that pastes used for the test should be proportioned and mixed to normal consistency, and the initial setting time was the elapsed time required to achieve a penetration of 25 mm. In this research, however, mix proportions shown in Table 3 were used for the pastes. Therefore, the initial setting determined is affected by the w/c and chemical admixtures used in the pastes.

## **RESULTS AND DISCUSSION**

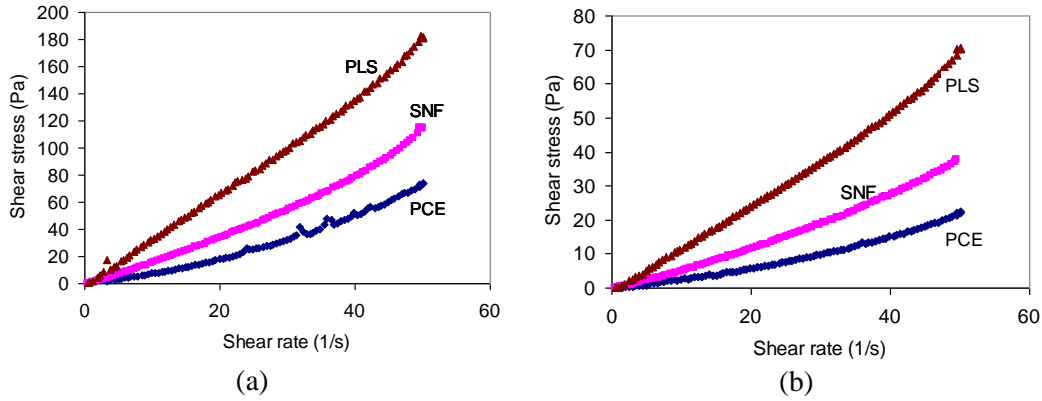
### **Effect of the Admixtures on the Change of Rheological Parameters with Time**

Shear stress vs shear rate graphs of the cement pastes with different admixtures at w/c ratios of 0.26 and 0.32 at 30 minutes are shown in Fig. 1 (a) and (b), respectively. Based on Herschel-Bulkley model ( $\tau = \tau_0 + K\dot{\gamma}^n$ ), yield stress  $\tau_0$  and parameters K and n of the cement pastes are summarized in Table 4. The R<sup>2</sup> of data fitting to the model was  $\geq 0.95$ . The yield stress of the cement pastes at 30 minutes was  $< 6 \text{ Pa}$ . For all the pastes samples, the power-law index “n” was  $> 1$  which indicates that these cement pastes behave as shear thickening materials, consistent with the observations for cement pastes with superplasticizers by Martin et al [2000].

The yield stress of the cement pastes increased with time due to cement hydration (Fig. 2). The time when the yield stress of the cement pastes increased sharply is summarized in Table 5. Although the yield stresses of the cement pastes with PCE and SNF admixtures were lower than that with PLS admixture at 30 minutes (Table 4), the yield stress of the formers increased with time in more rapid rates compared with that of the latter. The yield stress of the pastes with PCE and SNF increased significantly after about 1.3 to 2.5 hours, whereas that with PLS admixture increased significantly after about 7.9 to 11.3 hours depending on the w/c.

The difference on the yield stress change with time for the pastes with different superplasticizers is strongly influenced by retarding effect of the admixtures. Previous research [Sun et al. 2009] shows that PLS admixture has much stronger retarding effect

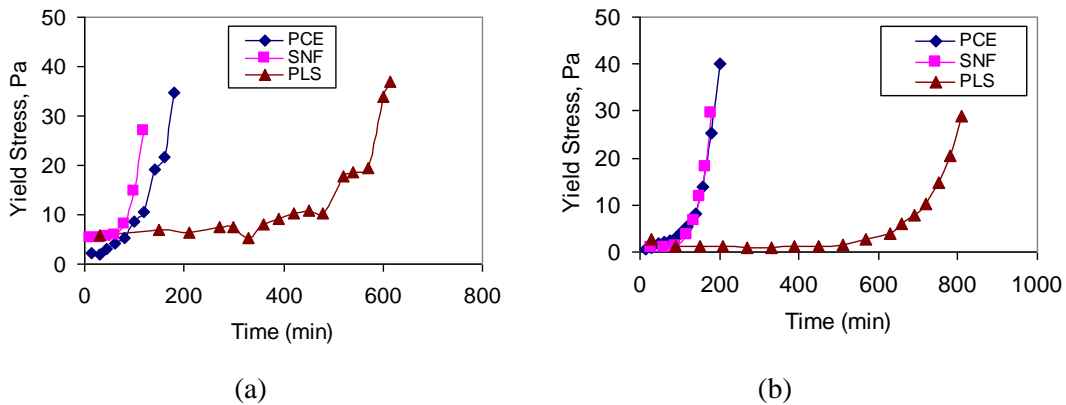
compared with that of SNF and PCE admixtures. This explains the longer time observed for the paste with PLS admixture before the yield stress increased significantly.



**Fig. 1 – Shear Stress vs Shear Rate for Cement Pastes at 30 min. (a) w/c = 0.26, (b) w/c = 0.32**

**Table 4 - Yield Stress and Parameters “K” and “n” Based on Herschel-Bulkley Model for Various Cement Pastes at 30 minutes**

Type of admixture	w/c	Yield stress, Pa	Consistency index “K”	Power-law index “n”
PCE	0.26	1.83	0.14	1.59
SNF		5.27	0.34	1.46
PLS		5.71	1.88	1.15
PCE	0.32	1.00	0.04	1.62
SNF		1.01	0.17	1.38
PLS		2.72	0.52	1.23



**Fig. 2 – Yield Stress Change with Time, (a) w/c = 0.26, (b) w/c = 0.32**

From Table 4, it was observed that the pastes with PLS admixture had higher “K” value, but lower “n” value compared with those of the corresponding ones with PCE and SNF

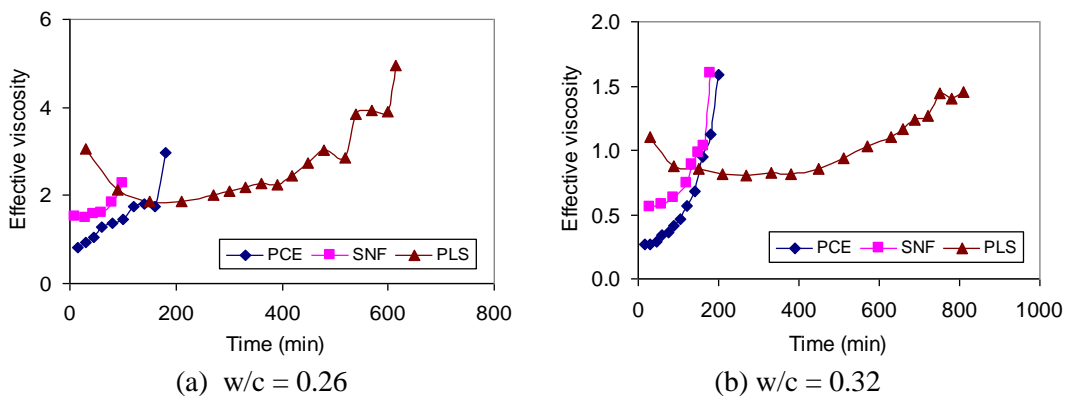
admixtures. The “K” and “n” values did not remain steady. The former generally trended up with time, whereas the latter generally trended slightly lower with time. Among the pastes with the three admixtures, the pastes with PLS had the lowest index “n” values followed by those with SNF, then PCE admixtures. The lower “n” values indicate lower shear thickening behaviour of the pastes at early age.

**Table 5 – Time When Yield Stress Increased Significantly and Initial Setting Time**

Type of admixture	w/c	Time when yield stress increase significantly, min	Initial setting time by Vicat test, min
No admixture		n.m.	90
PCE	0.26	110	300
SNF		75	230
PLS		475	990
No admixture		n.m.	140
PCE	0.32	150	415
SNF		120	290
PLS		680	1105

n.m. – not measured due to high yield stress

Figure 3 shows change of the effective viscosity of the cement pastes with time. The effective viscosity of the pastes with the PLS admixture was higher than the corresponding ones with PCE and SNF admixtures at 30 minutes. At w/c of 0.32, the effective viscosity of the cement pastes with PCE and SNF admixtures increased more quickly with time than that of the paste with PLS admixture. At w/c of 0.26, no data on effective viscosity for pastes with SNF and PCE admixtures were obtained after about 2 and 3 hours, respectively, due to the increase in the yield stress so that the measurement became difficult. However, the effective viscosity of the paste with PLS admixture remained relatively low until about 8 hours. This is also related to the stronger retardation effect of the PLS admixture. Comparing the cement pastes with w/c of 0.26 and 0.32, it seems that the former has higher effective viscosity than the latter.



**Fig. 3 – Effective Viscosity Change with Time (Shear Rate = 25 s<sup>-1</sup>)**

The viscosity of the cement pastes without admixtures generally increases with time due to cement hydration. However, it was observed from Fig. 3 that the effective viscosity of the pastes with PLS decreased slightly during the first hour, whereas the viscosity of the pastes with PCE and SNF increased with time. The difference is unexplained at this point.

The data on the yield stress and effective viscosity indicated that the paste with PLS admixture had longer workable time than that with PCE and SNF admixtures. This is particularly beneficial for concrete cast in hot weather conditions.

### **Workability Retention**

Workability retention of cement paste with superplasticizers is affected by dispersion mechanisms and retarding effect of the admixtures in addition to chemical and mineral composition of cement. For a given cement, the adsorption of the superplasticisers was strongly dependent on the type of admixtures used in the cement pastes [Sun et al. 2009].

From a previous study [Sun et al. 2009], it was found that in the paste with the PCE superplasticiser, almost all the superplasticiser was immediately adsorbed on cement particles, and remained adsorbed in the period of test. Due to the steric hindrance effect [Uchikawa et al. 1997; Flatt et al. 2000; Yoshioka et al. 2002; Bjornstrom and Chandra 2003], side chains of the polycarboxylate based superplasticiser prevent or reduce the agglomeration of cement particles, thus disperse the cement in the cement pastes. Loss of workability in the cement paste is probably related to cement hydration.

For the cement paste with the SNF superplasticiser, approximate 44% of the superplasticiser was adsorbed at 5 minutes, and the adsorption increased to about 51% at 60 minutes [Sun et al. 2009]. According to Collepardi [1998] and Hewlett [1998], naphthalene based superplasticisers neutralise surface charges of cement particles, cause all the surface to carry charges of like sign, thus disperse cement in suspensions through electrostatic repulsion. After the initial rapid adsorption, the superplasticiser adsorption continued on cement particles and its hydration products. However, the rate of adsorption was reduced with time. According to Kim et al [2000], for cement pastes with such superplasticisers, workability and workability retention are affected by the amount of free superplasticiser in the interstitial solution of the paste as well. Free naphthalene superplasticiser in solution may act as an additional repulsive barrier between cement particles which further improve the workability of the pastes. The increased adsorption and reduced SNF in solution with time reduces the additional repulsive barrier, and is thus partly responsible for the loss of workability in cement paste observed in addition to cement hydration.

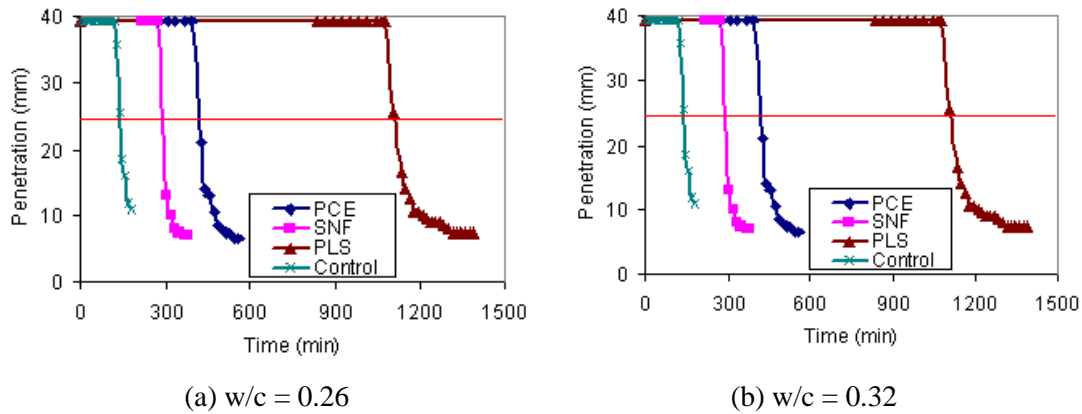
For the PLS superplasticiser, the adsorption was about 90% at 5 minutes and there was no significant change from 5 to 60 minutes [Sun et al. 2009]. According to Kauppi et al. [2005] the dispersion of cement by modified lignosulphonate superplasticisers may be attributed to combined effects of electrostatic repulsion and steric hindrance. The steric effect is believed to be caused by the cross-linked lignosulphonate molecules taking up a relatively large volume on the surface of cement particles [Ramachandran et al. 1998]. For these cement pastes, longer workable time observed is probably related to the stronger retardation effect of the admixture.

### **Effect of the Admixtures on Initial Setting Determined by Penetration Depth Method**

Penetration depth of the cement pastes with various admixtures determined by the Vicat needle test is shown in Fig. 4 in comparison to that of the corresponding control pastes. The initial setting time of the pastes with the penetration depth of 25 mm was summarized in Table 5. The results show that the initial setting times of the pastes with superplasticizers were longer than those of the control pastes due to the retardation of the superplasticizers. The results show that the initial setting of the pastes with w/c of 0.26 was slightly shorter than that with w/c of 0.32. In both cases, the setting was affected by the type and dosage of the superplasticizers used. The initial setting times of the pastes with PLS admixture was



more than 10 hrs longer than those with PCE and SNF admixtures. Although the pastes with PLS admixture had longer workable time, the longer setting time has to be taken into consideration in practice where early strength development is essential.



**Fig. 4 – Penetration Depth from Vicat Needle Test**

## SUMMARY AND CONCLUSIONS

Based on the experimental results, following conclusions may be drawn:

1. The shapes of the shear stress – shear rate curves indicated that the cement pastes were shear thickening materials. The pastes with modified lignosulphonate (PLS) admixture showed lower shear thickening behaviour than those with polycarboxylate (PCE) and naphthalene (SNF) admixtures.
2. Although the yield stresses and effective viscosity of the cement pastes with the PCE and SNF admixtures were lower than those with the PLS admixture at 30 minutes, the yield stress and effective viscosity of the formers increased more rapidly with time compared with the latter. This indicated that the paste with the PLS admixture had longer workable time which is related to the stronger retarding effect of the PLS admixture than the PCE and SNF admixtures.
3. The initial setting times of the pastes with the PLS admixture were much longer than those with the PCE and SNF admixtures.
4. Although the longer workable time is beneficial for hot weather concreting, the longer initial setting time with PLS admixture has to be taken into consideration where early strength development is essential.

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