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# EFFECT OF SUGAR-FREE LIGNOSULPHONATES ON CEMENT HYDRATION

ANALYZED

by V.S. Ramachandran

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## SOMMAIRE

L'aluminate tricalcique, le silicate tricalcique et le ciment Portland ont subi une hydratation selon un rapport eau: solide de 0.425 à 0.6 pendant une période allant de 15 minutes à 60 jours en présence de lignosulfonate de calcium commercial de 0 à 3%, de lignosulfonate de sodium sans sucre ou de lignosulfonate de calcium sans sucre. L'analyse des caractéristiques d'hydratation a été suivie d'une analyse thermique différentielle, d'une analyse thermo-gravimétrique, de la diffraction des rayons X et de la calorimétrie à conduction. Tous les lignosulfonates retardent l'hydratation du C<sub>3</sub>A et du C<sub>3</sub>S; plus l'effet retardateur est grand, plus la quantité d'adjuvant ajoutée est grande. Pour ce qui est de l'hydratation du ciment Portland, le retardement se produit au cours de la phase alite; on a constaté, toutefois, que le lignosulfonate commercial (0.3-0.5%) accélérerait les réactions primaires de la phase C<sub>3</sub>A. On a constaté une diminution importante de la quantité d'eau nécessaire pour une consistance normale pour tous les adjuvants. A de faibles concentrations, les trois adjuvants retardent la prise initiale et finale du mortier mais à des concentrations plus élevées, le lignosulfonate commercial favorise la prise rapide.

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## Effect of sugar-free lignosulphonates on cement hydration

By V. S. Ramachandran, Ottawa, Canada

### 1. Introduction

In concrete technology different types of admixtures are added to concrete to modify some of its physical and mechanical properties. One of the well-known admixtures is the calcium salt of lignosulphonic acid produced as a by-product of the wood pulp industry. The salts of lignosulphonic acid, such as calcium and sodium lignosulphonate, in small amounts, have the ability not only to retard the setting of cement but also to reduce the amount of water required for normal consistency.

Lignosulphonate is a complex polymer molecule of high molecular weight. It is derived from substituted phenyl propane containing hydroxyl, methoxyl, phenolic and sulphonic groups. The commercial lignosulphonates, however, are not pure and contain varying amounts of sugars such as mannose, glucose, xylose, galactose, arabinose and fructose. Sugars are known to be good retarders of setting of cement and hence the major part of the retarding action of a commercial lignosulphonate admixture is believed to be due to the wood sugars contained in it [ 1 - 3 ].

Recent studies have indicated that calcium lignosulphonate is an active admixture in concrete, interacting with the hydrating cement minerals [ 4 - 8 ]. Observations of the adsorption-desorption isotherms for the individual cement components in a solution of commercial calcium lignosulphonate, both in an aqueous and non-aqueous medium, show that lignosulphonate is irreversibly adsorbed by the  $C_3A$  and  $C_3S$  hydration products [ 4,6,7 ]. For example, in the hexagonal calcium aluminate hydrate-lignosulphonate- $H_2O$  system a study of the scanning loops indicated complete irreversibility and the formation of an interlayer complex. This complex had a higher surface area than the hexagonal phase and was more resistant to oxidation than the free

calcium lignosulphonate. The formation of the interlayer complex could explain the retardation or inhibition of the conversion of the hexagonal form to the cubic form of calcium aluminate hydrate. In the tricalcium silicate-calcium lignosulphonate -  $H_2O$  system [ 6 ], at low concentrations of lignosulphonate, perceptible sorption occurred on the hydrated  $C_3S$ . At higher lignosulphonate concentrations, in addition to the inhibition of hydration of  $C_3S$ , dispersion resulted. Both C-S-H and CH phases irreversibly adsorbed lignosulphonate. There was indication that lignosulphonate not only chemisorbed on the C-S-H surface but also entered the interlayer positions. These results suggested that the lignosulphonate molecule in a commercial sample should play a predominant role in dispersion, adsorption and retardation of hydration of cement. Thus, a lignosulphonate salt containing practically no wood sugars should be capable of influencing significantly the hydration and setting properties of cement, contrary to earlier opinions. Hence it was of interest to study the effect of sugar-free sodium and calcium salts of lignosulphonic acid on cement,  $C_3S$  and  $C_3A$  phases. A commercial calcium lignosulphonate containing sugar was also included in these studies for purposes of comparison.

### 2. Experimental

#### 2.1 Materials

The materials used in this work consisted of portland cement of low alkali type, tricalcium aluminate that was practically free of free lime and tricalcium silicate, containing 0.46 % free lime. Three types of lignosulphonates were utilized as admixtures in amounts varying between 0.1 and 3.0 %. They were: a commercial calcium lignosulphonate, sugar-free calcium lignosul-

phionate and sugar-free sodium lignosulphonate. The composition of the commercial lignosulphonate (produced by Lignosol Chemicals, Quebec 2, Canada) was as follows: moisture, 5 %, CaO, 9 %; ash, 17 %; S, 4.7 %; methoxyl, 7.2 %; sulphonate, 3.2 %; reducing bodies, 4.5 %. The reducing bodies included mannose, xylose, arabinose, glucose and galactose. Further characterization of this material was done by DTA, TGA and IR and has been published elsewhere [ 4 ].

Fractionation of Ca-lignosulphonate according to molecular size was performed by continuous diffusion using a Dowex 50WX2 resin bed in a calcium salt form [ 9 ]. The high molecular weight fraction of the calcium-base lignosulphonate was analysed by the chromatographic method and showed that it contained: sulphur, 6.21 %; ash, 11.1 %; methoxyl, 9.3 %; reducing bodies, 3.55 %. This fraction was sugar free and had a molecular weight of 6500 (weight average).

Sugar-free sodium lignosulphonate was obtained from the spray-dried commercial sodium lignosulphonate. Fractionation of the commercial sodium lignosulphonate was also performed on a Dowex 50WX2 bed in a sodium salt form. It had the following analysis: sulphur, 6.84 %; ash, 18.9 %; methoxyl, 9.46 %; reducing bodies, 1.85 %. The molecular weight was 4500 (weight average).

## 2.2 Techniques

DTA was carried out using a DuPont 900 thermal analyser. The rate of heating was 20° C/min. In each experiment a constant quantity of the sample ground to 100 mesh was packed at moderate pressure. Thermograms were obtained in a flow of N<sub>2</sub>.

TGA of the samples was carried out using a sensitive Cahn balance at a heating rate of 10° C/min, in a continuous vacuum. All the samples were compacted into a pellet before placing in the balance.

X-ray powder photographs were obtained with a Philips camera using a Cuk<sub>α</sub> source.

The rate of heat development during hydration was determined by a conduction calorimeter having a sensitivity of 20 mV/W.

The times of initial and final setting of mortar specimen were determined according to ASTM test method C403-70 [10].

Details of the above techniques have been described previously [ 11,12 ].

## 2.3. Procedure

Pastes of C<sub>3</sub>A and C<sub>3</sub>S were prepared using lignosulphonate in the range 0-3 % at water: solid ratios of 0.6 and 0.5, respectively. Each mix was placed in a tightly covered polyethylene container and rotated continuously over rollers. At specified intervals of time, varying between a few minutes and 60 days, each sample was placed in an excess of cold acetone, washed with cold acetone and subsequently evacuated for 24 h using a liquid air trap. The influence of lignosulphonates on the hydration of portland cement was carried out by curing the cement mortar specimens containing 0 %, 0.1 %, 0.3 %, or 0.5 % lignosulphonate at a water: solid ratio of 0.55, 0.54, 0.44 and 0.425, respectively. At specified intervals of time, the reaction was stopped by cold acetone and the hydrated cement was sieved out of the mortar using a 200-mesh sieve.

## 3. Results and discussion

### 3.1. Hydration of C<sub>3</sub>A

Addition of commercial calcium lignosulphonate is known to retard the hydration of C<sub>3</sub>A. Tricalcium aluminate hydrates with water to form initially hexagonal phases that eventually convert to the cubic hydrate. The rate of conversion of the hexagonal phases to the cubic phase in the presence of an admixture is conveniently followed by DTA [13]. Figs. 1, 2 and 3 show the thermograms of C<sub>3</sub>A hydrated in the presence of 0.1, 0.5, 1.0 or 3.0 % commercial calcium lignosulphonate (Cm-CLS), sugar-free calcium lignosulphonate (Sf-CLS) or sugar-free sodium

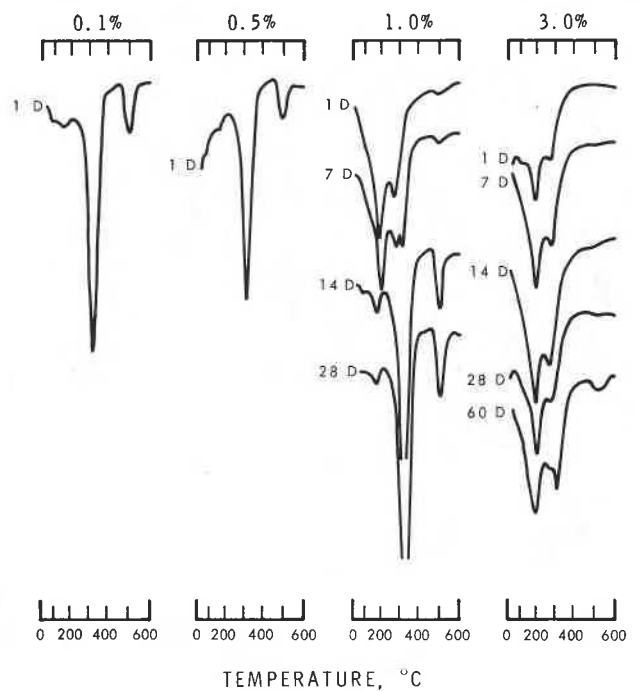


Fig. 1: DTA of C<sub>3</sub>A hydrated in the presence of commercial Ca-lignosulphonate

lignosulphonate (Sf-NLS), for periods ranging from 1 to 60 days. These samples exhibit a number of endothermal effects which can be attributed to various factors as follows. The peak at about 100° C is due to the desorption of adsorbed water. The endothermal effects at about 200 and 250-280° C are ascribed to the dehydration of the hexagonal phases C<sub>2</sub>A H<sub>8</sub> - C<sub>4</sub>AH<sub>13</sub>. The effects at about 300 and 500° C represent a stepwise dehydration of the cubic phase C<sub>3</sub>A H<sub>6</sub>.

The thermal behaviour of C<sub>3</sub>A hydrated in the absence of admixtures (not shown in the figure) indicates, even at 15 min, a large endothermal effect at 300° C followed by another at about 500° C. This is due to the presence of the cubic phase in this sample. In the presence of 0.1 % admixture there is a slight retardation effect in the early periods of hydration but at 1 day in all samples the cubic phase is the only dominant phase present. At an addition of 0.5 %, Sf-NLS seems to be the best retarder of the three. This is evident from the presence of a large amount of hexagonal phases at 1 day with this admixture (Fig. 3). At this

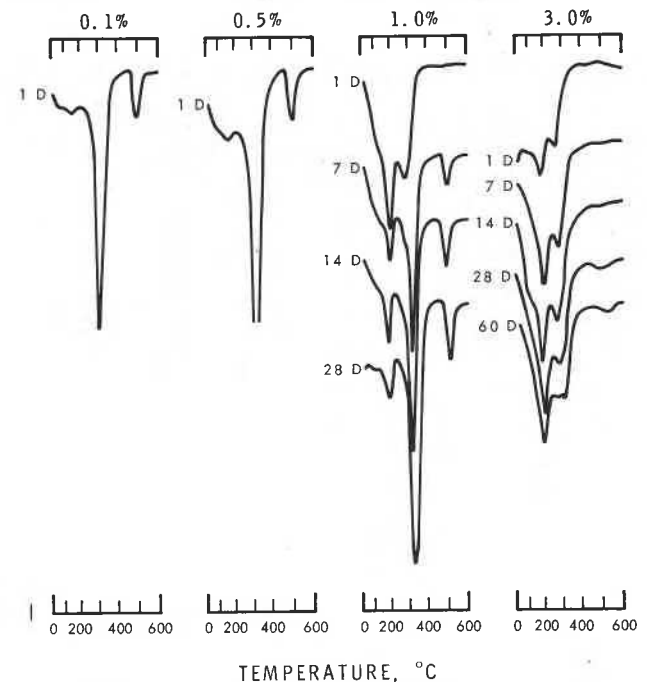


Fig. 2: DTA of C<sub>3</sub>A hydrated in the presence of sugar-free Ca-lignosulphonate

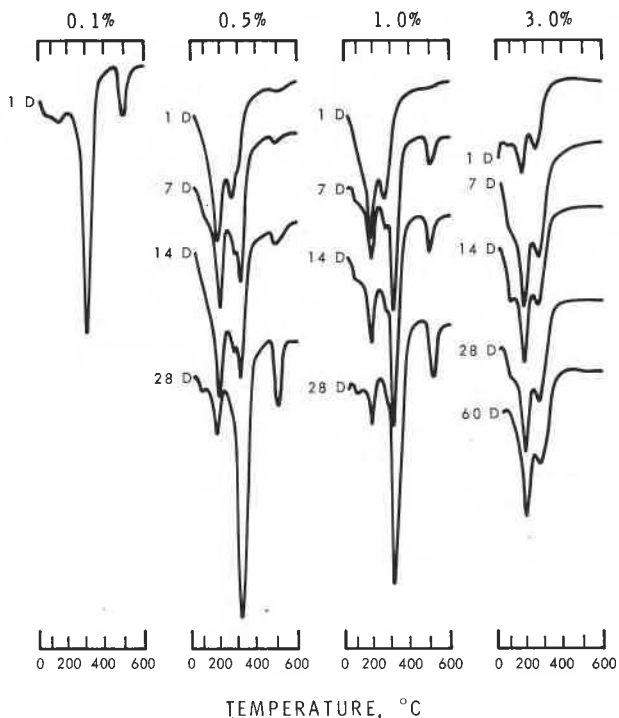


Fig. 3: DTA of  $C_3A$  hydrated in the presence of sugar-free Na-lignosulphonate

concentration an almost complete conversion to the cubic phase occurs only at 28 days. In the presence of 1.0% admixture the conversion reactions are further retarded. At 1 day of hydration only the hexagonal phases are present. With further curing the conversion reactions are enhanced and at 14 days the hexagonal phase is substantially converted to the cubic phase. At an addition of 3% lignosulphonate, a much more efficient retardation of hydration results. At 1 day only, a small fraction of  $C_3A$  seems to have hydrated. The degree of hydration increases with time and only a small amount of conversion to the cubic form occurs even at 60 days, with admixtures Cm-CLS and Sf-CLS. These results demonstrate that the sugar-free lignosulphonates are at least as efficient retarders of the hydration reactions in  $C_3A$  as the commercial lignosulphonate. The efficiency of the retardation increases as the amount of admixture is increased.

Thermogravimetric analysis was done on all samples hydrated from 1 to 28 days. The relative amounts of hydration products formed were determined by weight losses occurring over a temperature range corresponding to the DTA curves. There was generally a good agreement between the TGA and DTA results. For example, with 0.5% Cm-CLS hydrated to 1 day only, the cubic phase was detected and the loss in weight for this compound corresponded to an amount of 47.2%. With 3% Sf-NLS hydrated for 1 day, the weight loss below 250°C represented the presence of about 19.4% hexagonal phase (in terms of  $C_4A \cdot H_13$ ).

Many of the samples were also examined by the X-ray diffraction technique. The unhydrated  $C_3A$  showed typical strong lines of  $C_3A$  at 2.7 and 1.9 Å. In the presence of 0.5% Cm-CLS, at 1 day, the peaks due to  $C_3A$  diminished and strong peaks at 5.13, 2.8 and 2.3 Å, representing the formation of the cubic phase, appeared. However, with 3% Cm-CLS, at 1 day, broad lines at about 10.5 and 7.9 Å could be ascribed to the presence of the hexagonal phases. The diffraction patterns of samples containing Sf-CLS were generally similar to those containing Cm-CLS. The specimens prepared with Sf-NLS showed some differences. For example, at 1 day with 0.5% Sf-NLS, peaks at about 7.9 and 2.86 Å, corresponding to the presence of substantial amounts of hexagonal phases, predominated. At this period only a small amount of the cubic phase was formed. All the samples with 3% lignosulphonate showed lines representing the hexagonal phases even at 28 days. The above results are in good agreement with those of DTA and TGA. It appears, therefore, that the sugar-free lignosulphonates form interlayer complexes just as the commer-

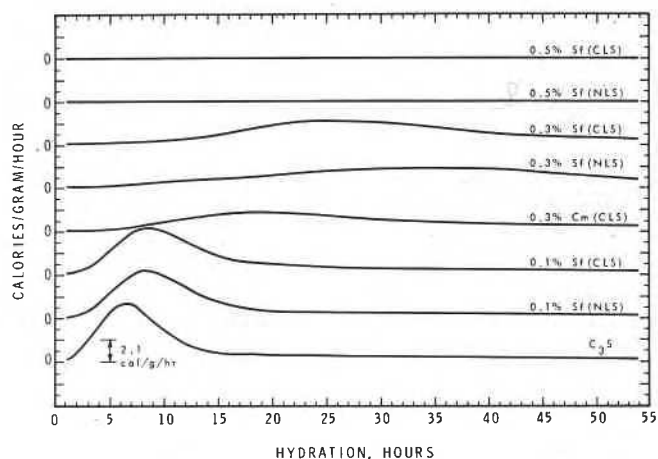


Fig. 4: Conduction calorimetric curves of tricalcium silicate hydrated in the presence of lignosulphonates

cial lignosulphonate [7] and retard the conversion of the hexagonal to the cubic form in the  $C_3A-H_2O$ -lignosulphonate system.

### 3.2 Hydration of $C_3S$

The influence of lignosulphonates on the hydration of  $C_3S$  was followed by conduction calorimetry (Fig. 4). In the absence of an admixture,  $C_3S$  shows a hump at about 7 h representing the completion of the accelerated stage of hydration. After about 15 h, the rate of heat development is very slow and this corresponds to the decay period [14]. By the addition of 0.1% Sf-CLS or Sf-NLS, the induction period is increased from about 1 1/2 h to about 2 h and the rate of heat development is decreased. The time of occurrence of the peak increases from about 7 h to 8–9 h, thereby indicating that the addition of 0.1% Sf-lignosulphonate results in the retardation of the hydration of  $C_3S$ . At an addition of 0.3% lignosulphonate, further reduction in the rate of hydration is evident, the Sf-NLS being the most effective retarder. At 0.5% Sf-NLS or Sf-CLS, the hydration of  $C_3S$  is almost completely inhibited. Previous work has shown that at 0.5% addition, Cm-CLS also inhibits the hydration of  $C_3S$ .

### 3.3 Hydration of Cement

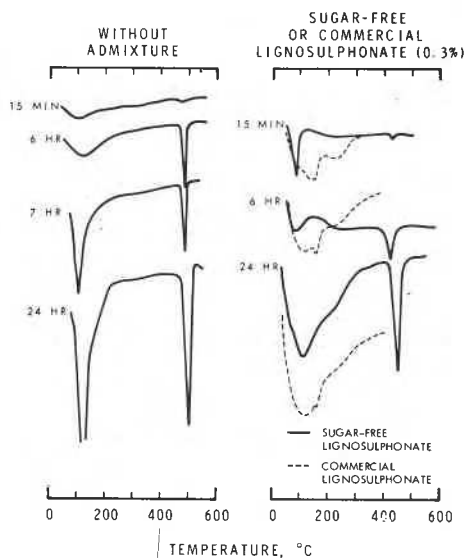
Lignosulphonates when added to concrete reduce the water requirement for a given consistency and also extend the setting times. Table I gives the water reductions and changes in the setting times that occur when different amounts of lignosulphonates are added to the mortar (1 : 3 = cement : sand). The addition of 0.1% admixture is sufficient to extend the initial and final setting times by 2 and 3 h, respectively. At 0.3 or 0.5% dosage, the sugar-free lignosulphonates extend both the initial and final setting times substantially. Addition of 0.3 or 0.5% Cm-CLS, however, results in the quick-setting phenomenon. This is probably due to the modification of the early hydration reactions of  $C_3A$ , as explained later. Quick-setting phenomena have been observed in mortars containing sucrose or water reducers [15, 16]. There is no apparent difference between Sf-CLS and Sf-NLS in their effect on water reduction or set-retarding characteristics; at 0.5%, water reduction is 22.7%.

The influence of different amounts of lignosulphonate on the hydration of cement was followed by DTA and conduction calorimetry. A few representative DTA curves are shown in Fig. 5. The reference cement containing no admixture exhibits a broad endothermic effect below 200°C representing the formation of both ettringite and C-S-H. The endothermic effects increase in intensity as the hydration period is increased. The effect between 450–500°C is caused by the dehydration of  $Ca(OH)_2$  and its intensity indicates the extent of hydration of the  $C_3S$  component of cement. The cement hydration in the presence of admixtures (both commercial and sugar-free types) is retarded. It is indicated by the lower intensity of the  $Ca(OH)_2$  decomposition peak. The low temperature effects below 300°C in the presence of Cm-CLS are significantly dif-

**TABLE 1**  
Water reduction and setting characteristics of mortar containing lignosulphonates

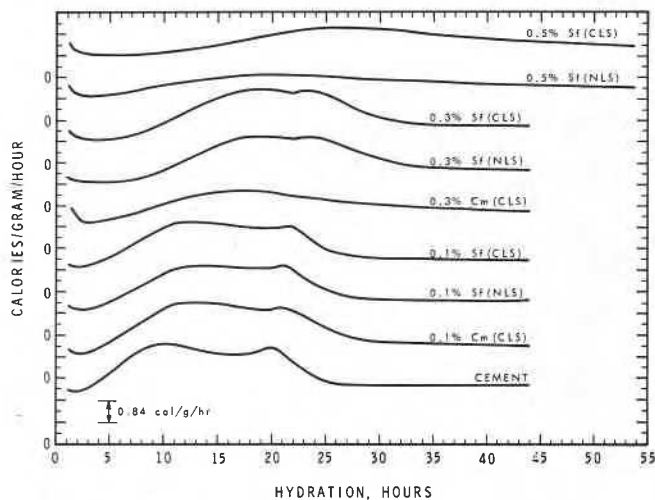
Art des Zusatzes Type of admixture	Menge des Zusatzes Amount of admixture %	W : Z Water/ Cement ratio	Erstarr.- Beginn Initial set (h)	Erstarr.- Ende Final set (h)
Nichts / Nil	Nil	0,550	5	9
Commercial *) Ca-lignosulphonate	0,1	0,540	7	12
Sugar-free **) Na-lignosulphonate	0,1	0,540	7	12
Sugar-free Ca-lignosulphonate	0,1	0,540	7	12
Commercial Ca-lignosulphonate	0,3	0,440	quick set***)	13,5
Sugar-free Na-lignosulphonate	0,3	0,440	12	15
Sugar-free Ca-lignosulphonate	0,3	0,440	14	16,5
Commercial Ca-lignosulphonate	0,5	0,425	quick set	22
Sugar-free Na-lignosulphonate	0,5	0,425	23	28
Sugar-free Ca-lignosulphonate	0,5	0,425	22	27,5

\*) Commercial = handelsüblich  
 \*\*) Sugar-free = zuckerfrei  
 \*\*\*) quick set = Schnellbinder



**Fig. 5:** DTA of cement hydrated in the presence of lignosulphonates

ferent from those in the presence of sugar-free lignosulphonates. With sugar-free lignosulphonate, ettringite is formed initially (peak at about 100° C) with a broadening effect at 6 h due to the formation of C-S-H phase. At 15 min, cement containing Cm-CLS shows broad endothermal valley with three peak effects in the temperature range 100 – 300° C. The general features of this curve may be observed even at 24 h. These may be caused mainly by the presence of low sulphoaluminate hydrate (160° C) and C-S-H. Probably 0.3 % Cm-CLS accelerates the



**Fig. 6:** Conduction calorimetric curves of cement hydrated in the presence of lignosulphonates

formation of ettringite and its conversion to low-sulphoaluminate hydrate within minutes after contact with water. The quick set caused by 0.3 % Cm-CLS in the mortar may be related to this acceleration effect [ 15, 16 ] (Table I). The quick set is not observed with sugar-free lignosulphonates as they initially form ettringite that is slowly converted to the low sulphate form.

The conduction calorimetric curves of cement with 0, 0.1, 0.3 and 0.5 % lignosulphonate are given in Fig. 6. As soon as the cement comes into contact with water an exothermal heat effect initially occurs due to the heat of wetting, hydration of free lime and early formation of ettringite. These are not shown in the figure. The cement containing no admixture exhibits a peak at about 10 h caused by the hydration of the alite component of cement and formation of increasing amounts of ettringite. Another peak at about 20 h is generally attributed to the transformation of the high sulphate form of calcium sulphoaluminate hydrate (ettringite) to the monosulphate form. At 0.1 % addition of the admixture there is a decrease in the rate of reaction in the first few hours which is evident by the decreased rate of heat evolution. In the first 15 h of hydration, the rate of heat evolution is generally lower with the cement containing sugar-free lignosulphonates. A significant decrease in the rate of hydration occurs in the presence of 0.3 – 0.5 % sugar-free lignosulphonates. An absence of the second peak in the presence of 0.3 % Cm-CLS would indicate that ettringite-mono-sulphate conversion has occurred at very early periods. Its significance in the quick-setting phenomenon has already been discussed.

#### 4. Conclusions

The sugar-free calcium and sodium lignosulphonates in small amounts are at least as effective as the commercial lignosulphonate in water-reducing capacity and retardation of initial and final setting characteristics of cement. At higher concentrations, the commercial lignosulphonate causes quick set due to the presence of sugars, whereas the sugar-free lignosulphonates extend the setting times significantly. At different concentrations, the sugar-free and commercial lignosulphonates retard the hydration of portland cement, tricalcium silicate and tricalcium aluminate.

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