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The role of calcium ions and lignosulphonate plasticiser in the hydration of cement

L.H. Grierson[a,*], J.C. Knight[b], R. Maharaj[a]

[a]Department of Chemistry, University of the West Indies, St. Augustine, Trinidad and Tobago, W.I.
[b]Department of Physics, University of the West Indies, St. Augustine, Trinidad and Tobago, W.I.

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Abstract

Experiments involving equilibrium dialysis, conductivity, X-ray diffraction analysis (XRD), differential thermal analysis (DTA) and isothermal titration calorimetry (ITC) have been carried out to investigate the role of calcium ions and polymeric plasticisers in cement/admixture hydration. Results from a study of lignosulphonic acid, sodium salt, acetate as a plasticiser shows that a plasticiser has dual role; one mainly as a kinetic inhibitor (poison) in cement hydration mechanism and the other as a dispersant. Evidence of a weak Ca^{2+} binding to lignosulphonate sulphonic moieties was found at low ionic strengths of 0.1 M using ITC. No evidence of formal Ca^{2+} binding to lignosulphonate sulphonic acid moieties was found using equilibrium dialysis at higher ionic strength of 1 M (ionic strengths of 0.4 M are typically found in Portland cement pore solution), as is often suggested in cement/admixture literature.

Keywords: Portland cement; Admixtures; Hydration; Kinetics; Thermodynamic calculations

1. Introduction

Cement admixtures are used as plasticisers to reduce the water requirement in mixing concrete. There are a variety of chemical admixtures available, which vary much in composition. Among the plasticisers lignosulphonate base work like retarders. It prolongs the hydration period of cements. It is reported that the lignosulphonate base plasticisers greatly modify the initial rheological properties and the final compressive strength of cement base materials [1,2]; however, the mechanism of interaction is not clearly understood.

Two main models have been proposed to explain cement hydration. Model I, with many variants, evolved from a number of studies, as documented by Taylor [3]. According to this model, the mechanism of hydration is based on the effect of saturation/supersaturation of Ca^{2+} ion on the hydration of C_3S particles, via assisting a morphological change from an impervious calcium silicate gel to its permeable crystalline form. Model II, for the hydration of cement (containing gypsum), proposed by Billingham and Coveney [4] and Billingham and Needham [5,6] and later substantiated by Hughes et al. [7], suggests a ‘‘clock-like’’ mechanism for the hydration process. Here, the induction period is associated with the formation of water-impermeable ettringite gel (from C_3A) on the C_3S surface and its transformation to water-permeable crystalline form. The advantage of Model II compared with Model I is that it links C_3S hydration and ettringite formation.

Chandra et al. [8–10], among others [11–14], have suggested that the hydration retardation effects of superplasticisers in cement/cement admixtures is due to the interaction of Ca^{2+} ions [or $Ca(OH)_2$ particles] formed during C_3S hydration with sulphonate ions in superplasticisers, or due to superplasticiser micellisation of water available for the hydration of the silicates. Another hypothesis, based on the work by Monosi et al. [15,16] studying the effects of additive glucose, gluconate and sodium lignosulphonate on the systems C_3S, C_4AF and $C_3A/C_4AF/CaSO_4$, holds that their action causes the acceleration of early ettringite gel formation or inhibition of the conversion of ettringite to monosulphonate. Later work by

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* Corresponding author. Tel.: +1-868-662-6013; fax: +1-868-645-3771.

E-mail address: lebertgrierson@hotmail.com (L.H. Grierson).

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Hughes et al. [7] suggests that released Ca^{2+} ions at supersaturated concentration could act as an inhibitor of the crucial ettringite (water-impermeable gel form) to ettringite (water-permeable crystalline form) step and hence cause the induction phase in cement (containing gypsum) hydration process. This is consistent with the idea of Billingham and Coveney [4], who suggested that plasticisers/superplasticisers could have a similar hydration inhibition role as Ca^{2+} ions.

Although most studies, especially the earlier ones, have favoured Model I, the exact mode of action depends on the specific plasticiser type or specific plasticiser. Nevertheless, the results reported are qualitative and not quantitative. This paper describes the binding action of Ca^{2+} ions on lignosulphonic acid, sodium salt and acetate quantitatively. Quantification was done in terms of the thermodynamics parameters nK_{ass}, ΔG, ΔH and ΔS, determined by equilibrium dialysis. In addition, isothermal titration calorimetry (ITC), conductivity, X-ray diffraction analysis (XRD) and differential thermal analysis (DTA) experiments were conducted to study the action of lignosulphonic acid, sodium salt, acetate on Trinidad Portland cement. The results are discussed alongside those reported earlier by Taylor [3], Chandra and Flodin [10] and Billingham [4–6].

2. Experimental

2.1. Equilibrium dialysis

The calcium ion binding to the lignosulphonic acid, sodium salt, acetate, LS (a product supplied by Sigma-Aldrich) was determined at temperatures of 8, 15, 25 and 35 °C using Klotz equilibrium dialysis method [17]. This involved mixing calcium nitrate (source of the Ca^{2+} ions) with the plasticiser inside a membrane. The ionic strength on both sides of the membrane was kept constant. After the system equilibrated, the concentration of Ca^{2+} was determined by atomic absorption spectrophotometry, followed by the calculation of the binding (or association) constant K_{ass} between Ca^{2+} and LS using the Klotz equation

$$\frac{1}{r} = \frac{1}{nK_{ass}c} + \frac{1}{n} \tag{1}$$

where n is the number of binding sites (i.e., $-SO_2OH$ groups) per unit ligand, r is the number of moles of metal bound to 1 mol of polymer and c the free-metal concentration. If complexation occurs, a plot of $1/r$ against $1/c$ should yield a straight line, with slope $1/nK_{ass}$ and intercept $1/n$; hence, the product nK_{ass} can be determined. However, extrapolation to obtain the intercept $1/n$ produces large errors in the estimation of n; therefore, nK_{ass} was chosen as the equilibrium constant in this study.

The enthalpy, ΔH, of binding of Ca^{2+} ions to LS was determined from the slope of a van't-Hoff-type plot of $\ln(nK_{ass})$ against $1/T$, where T is temperature. ΔG, the free energy of binding, was calculated form the equilibrium constant nK_{ass} ($\Delta G = -\mathrm{RT}\ln nK_{ass}$) while the entropy, ΔS, of binding was calculated from the difference between the ΔG and ΔH values [$\Delta S = (\Delta H - \Delta G)/T$].

2.2. Conductivity study

The conductivity of various Trinidad Portland cement pastes (water/cement ratio = 2) containing 0%, 0.05% and 0.5% of the plasticiser (LS) was measured using the method of Maximilien et al. [18]. This involved the measurement of the electrical conductivities of the various cement pastes in the presence of varying amounts of the additive, monitored using a Cole Palmer analyzer model #5800-05. In each experiment, cement and solution (the water/solid ratio = 2) containing the different amounts of LS were thoroughly mixed for 10 s using a vortex mixer. The paste was immediately placed in a 250-ml beaker, and the conductivity probe (cell constant 0.1) was immersed in the solution (paste). The experiments were conducted at 25 °C, and the electrical conductivity measurements taken at 2-min intervals over 3 h (to avoid the setting of the cement on the electrode). Change in conductivity with time was determined by subtraction of the initial conductivity of the additive solution alone from those of the cement/additive paste at all intervals.

2.3. Isothermal titration calorimetry

Calorimetric study for the binding of Ca^{2+} to LS was done at two pH values (7.0 and 7.5) and at 25 °C using a VP-ITC. The experiment involved 25 sequential injections, at 3-min intervals, of 10-μl aliquots of LS (approximately 20–25 mM $CaCl_2$ prepared in buffer) solution into the stirred calorimeter cell containing LS of concentration 2.2 mg/ml in buffer [the buffers used were TRIS acetate (0.1 M, pH 7.0 and 7.5), MOPS (3-[*N*-morpholino]propanesulfonic acid hemisodium salt) (0.1 M, pH 7.0)]. This produced a series of exothermic or endothermic heat pulses, which, after correction for appropriate control experiments, under identical condition, were analysed using Origin 5.046 software to give K_{ass} (association equilibrium constant), K_{diss} (dissociation equilibrium constant) and ΔH (calorimetric enthalpy) [19].

2.4. XRD and DTA analysis

For the XRD and DTA studies, separate samples containing plasticiser concentrations of 0%, 0.05%, 0.1%, 0.3% and 0.5% of the weight of the cement (50 g) were prepared by forming pastes with the plasticiser dissolved in 25 ml deionized water. The hydration process was stopped after 2, 7 and 14 days by grinding the samples to powder, followed

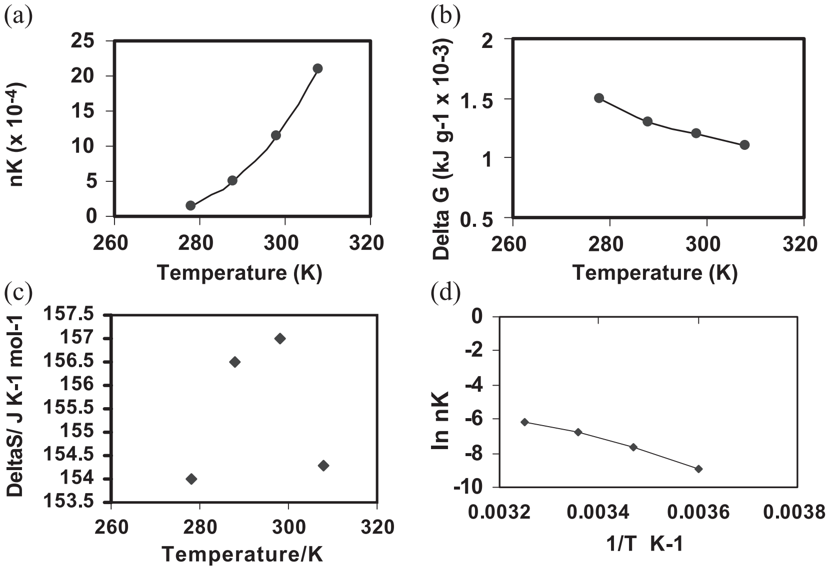

Fig. 1. Variation of the binding parameters from equilibrium dialysis experiments (a) nK_{ass}, (b) ΔG, (c) ΔS with temperature for binding between calcium ions and lignosulphonic acid ligands and (d) $\ln nK_{ass}$ vs. $1/T$.

by immersing in acetone. Subsequently, XRD was done on the powders using CuKα radiation and Ni filter in a Philips diffractometer operated at 40 kV and 20 mA. DTA was done using a DuPont Instrument Series 990 in conjunction with a 910 differential scanning calorimeter over the temperature range 20–1000 °C at a heating rate of 20 °C/min.

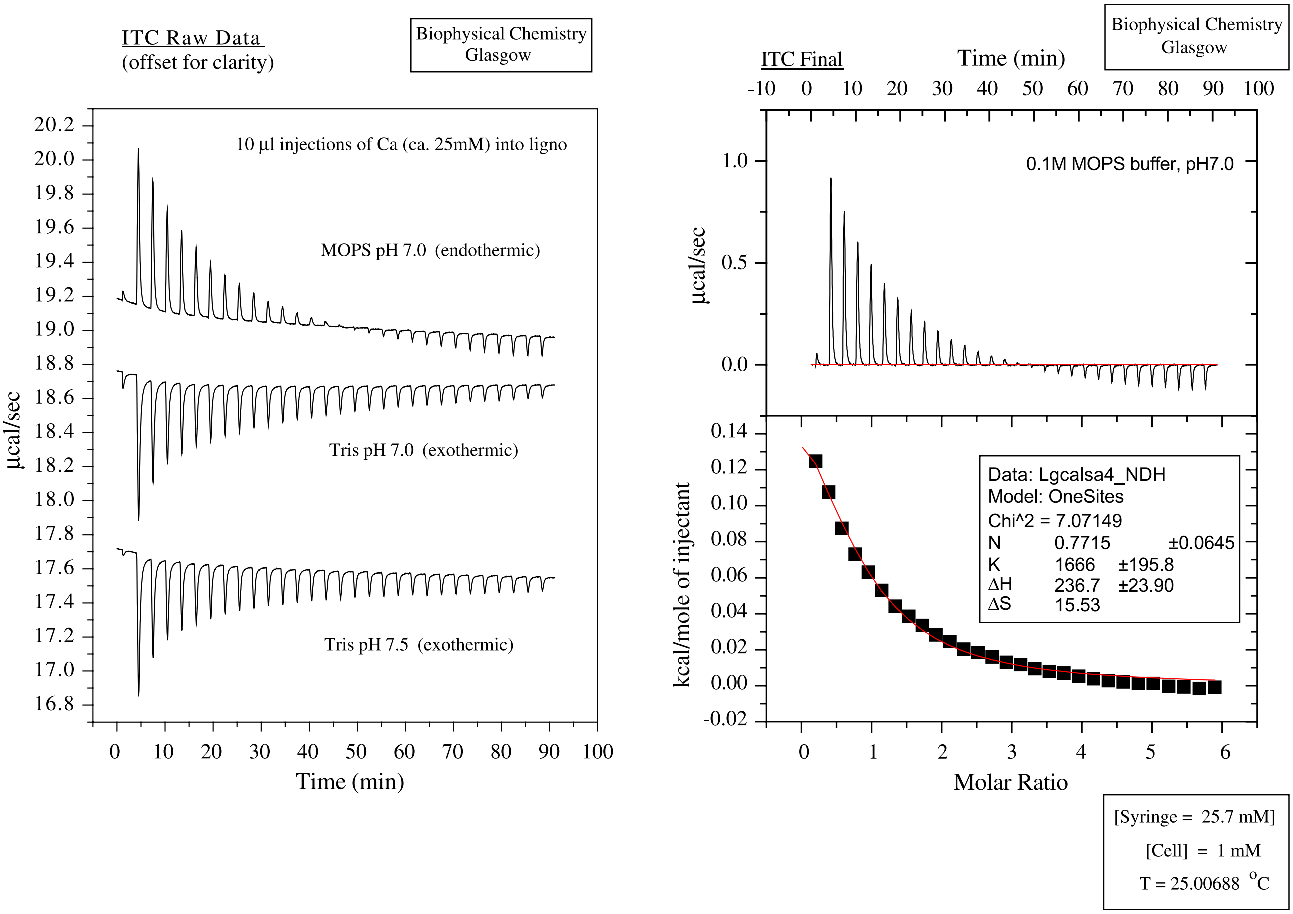

Fig. 2. Calcium ions binding to the lignosulphonic acid ligand using ITC, using 25 × 10 µl injections of calcium ions to lignosulphonic acid, sodium salt and acetate.

3. Results and discussions

Fig. 1 shows the temperature dependence of nK_{ass}, ΔG, ΔH and ΔS for the binding of calcium ions to LS. As can be seen, nK_{ass} increased with increasing temperature, while ΔG, ΔH and ΔS all exhibited positive values but decreased with increasing temperature. However, the actual values of the binding constant nK_{ass} are extremely small, ranging between 1.42×10^{-4} and 21×10^{-4} over the temperature range studied. Furthermore, the ITC data indicate a K_{ass} value of $\approx 1000\ \mathrm{M}^{-1}$ ($K_{\mathrm{diss}} \approx 1$ mM), suggesting very weak Ca^{2+} binding (Fig. 2). This weak binding would be expected to be much smaller or absent at higher ionic strengths (e.g., 1 M tetrabutyl ammonium bromide used in the dialysis experiment) and thus was not picked up in equilibrium dialysis experiments. In addition, as is well documented (e.g., Ref. [20,21]), ionic binding can be totally inhibited at high ionic strengths due to electrostatic screening, reducing coulombic binding.

Conductivity studies show that up to 30 min after preparing the cement/plasticiser paste, there is a positive change (i.e., an increase compared with time zero) in the conductivity with optimum occurring after approximately 6 min (Fig. 3). This positive change is associated with Ca^{2+} ion release [18]. Furthermore, in this time interval, the magnitude of the change for the samples containing 0% and 0.05% plasticiser is similar but greater than for the sample with 0.5% plasticiser. This suggests that while low concentrations of the plasticiser has little or no control over the release of Ca^{2+} ions into the solution at concentrations of the order of 0.5% or more, it acts to inhibit Ca^{2+} release. Taken together, these observations seem to reflect that in the 0- to 30-min time interval, there is competition between the principal hydration reaction and plasticiser-induced inhibition of Ca^{2+} release, with the inhibition process dominating at 0.5% plasticiser concentration. Furthermore, the inhibition probably poisons the process of crystalline ettringite formation and hence reduces initial C_3S hydration. For

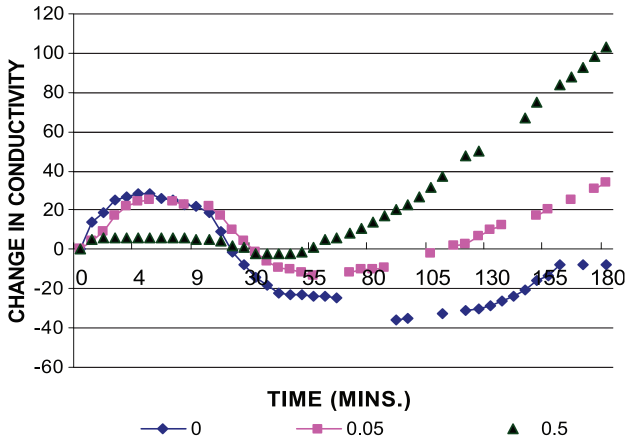

Fig. 3. The effect of plasticiser concentration on the conductivity of the cement/admixture paste.

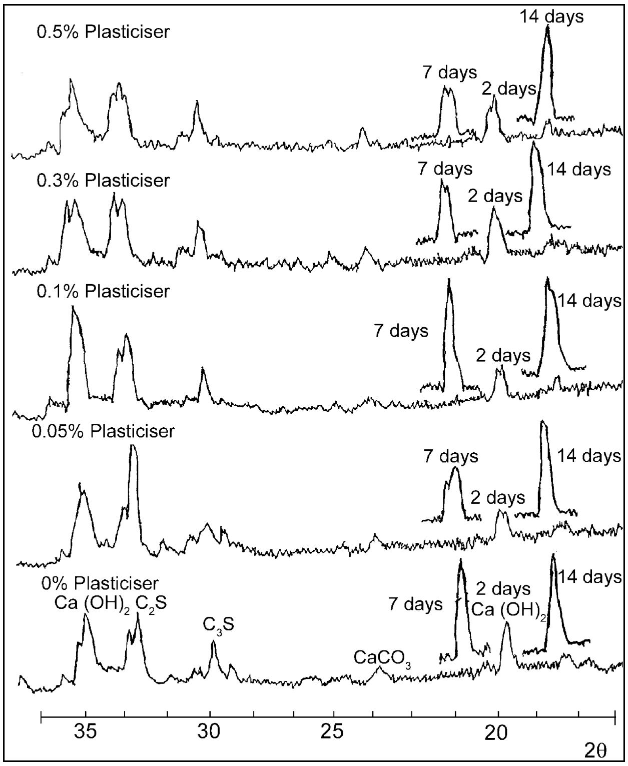

Fig. 4. Normalised XRD profiles of 7-, 14- and 28-day aged samples containing the indicated concentrations of plasticiser. The $Ca(OH)_2$ peaks at 18.5° 2θ peaks, offset to compare intensity after the hydration times indicated.

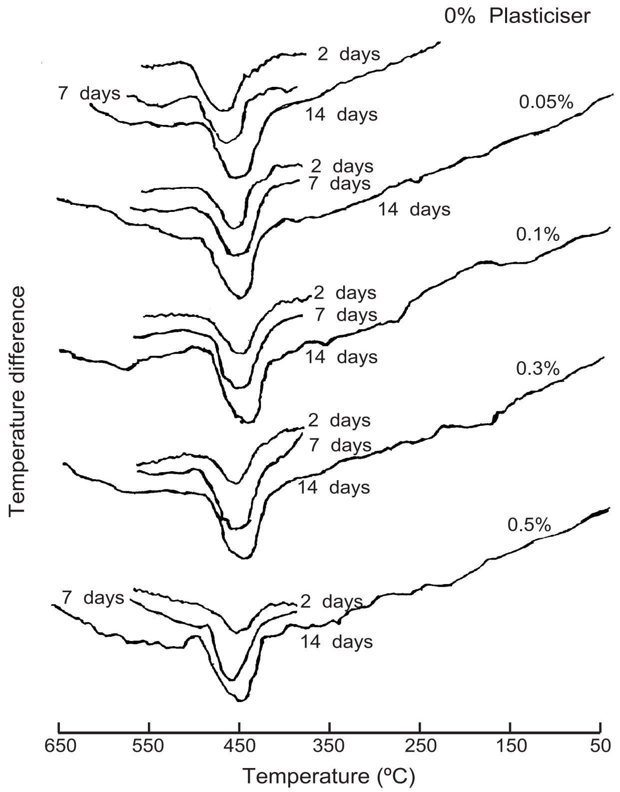

Fig. 5. DTA profiles of 7-, 14- and 28-day aged samples containing the indicated concentrations of plasticiser.

aging times greater than approximately 30 min, the reason for the trend in variation of the conductivity (Fig. 3) is not clear but is perhaps related to the complexities of the reactions taking place.

The XRD study shows that the intensity of the $Ca(OH)_2$ peak (related to calcium ions) generally increased with hydration time (Fig. 4). However, while the effect of increasing the plasticiser content is not readily deduced from the XRD profiles, it becomes evident from the DTA profiles (Fig. 5). In particular, the endothermic peak at approximately 450 °C (corresponding to decomposition of formed calcium hydroxide crystals) decreased with increasing plasticiser concentration after 2 days aging, thereafter (7 and 14 days) tending to increase. Consistent with the results of the conductivity study, this suggests that in the early stages of hydration, LS acts as an inhibitor. Thus, in agreement with the Billingham et al. model, the higher the inhibitor concentration, the greater the retardation of hydration and, hence, the smaller the amount of calcium hydroxide after 2-day hydration. Based on Billingham model (Model II), it is only when the inhibitor effect is exhausted that the ettringite morphology changes from the gel form to the crystalline form. At this stage, the principal hydration reaction is renewed, allowing normal hydration, so that after 7 and 14 days, the effect of inhibition on hydration is not observed.

The increase in the $Ca(OH)_2$ peaks after the inhibitor effect is exhausted indicates an increased hydration of C_3S. This may be explained on the basis of LS (plasticiser) having a dual role: In the initial stages of hydration, it functions as an inhibitor, and in the latter stages, as a dispersant. A consequence of this dispersive behaviour is an increased state of deflocculation in the paste and, hence, a more homogeneous paste with more available particle surface area. Then, since the growth of the hydrate particles is largely a surface absorption phenomenon, one can expect that increasing the amount of LS (plasticiser) incorporated in the system will increase the degree of dispersion and, hence, the amount of $Ca(OH)_2$ and, thus, hydrate C_3S formed.

4. Conclusions

Many mechanisms have been proposed as to the nature of the effect of admixtures on the properties of cements. Much confusion has arisen due, in part, to the complex nature of cement hydration. However, it seems evident that there is an intricate balance between the complex chemical reactions that occur during hydration, the mineral composition of the cement and the effect of the admixture on the hardening of the cement paste. The results presented in this paper show that at low ionic strengths, Ca^{2+} ions bind weakly to LS but not at high ionic strengths. Since high ionic strengths of 0.4 M are present in Portland cement pore solution [22], it can be expected that in the case of plasticiser, lignosulphonic acid, sodium salt, acetate (LS) and, possibly, other plasticisers, Ca^{2+} ion binding to plasticiser is not significant as previously suggested by proposed models for cement/cement admixture hydration. However, the Billingham et al. model (Model II), in which the plasticisers or admixtures (e.g., phosphate ions) functions as an inhibitor, can explain the result of the crucial morphology change from ettringite gel to ettringite crystalline during hydration. In addition, a plasticiser can function as a dispersant, a role that commences immediately after mixing but manifested only during the latter stages of hydration, thereby improving the hardening properties of hydrated cements.

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