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by

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INTERACTION OF CALCIUM LIGNOSULFONATE WITH TRICALCIUM SILICATE, HYDRATED TRICALCIUM SILICATE, AND CALCIUM HYDROXIDE

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(Communicated by P. J. Sereda)

ABSTRACT

Tricalcium silicate, bottle-hydrated tricalcium silicate and calcium hydroxide were each treated with 0.015-1.0% calcium lignosulfonate (CLS) using water or dimethyl sulfoxide. At low CLS concentrations C_3S hydrates and irreversibly adsorbs CLS. At concentrations beyond about 0.25-0.35% the hydration of C_3S is inhibited. Bottle-hydrated C_3S adsorbs CLS irreversibly in both the aqueous and the non-aqueous media. The CH phase also irreversibly adsorbs CLS. Dispersion and the formation of basic CLS are indicated.

SOMMAIRE

On a traité le silicate de tricalcium, le silicate de tricalcium hydraté en bouteille et l'hydroxyde de calcium avec 0.015-1.0% de lignosulfonate de calcium (LSC) au moyen d'eau ou de sulfoxyde de diméthyle. Pour de faibles concentrations de LSC, le C_3S devient un hydrate et adsorbe le LSC irréversiblement. Les concentrations de plus d'environ 0.25-0.35% empêchent l'hydratation du C_3S. Le C_3S hydraté en bouteille adsorbe le LSC irréversiblement dans les milieux aqueux et non aqueux. La phase CH adsorbe également le LSC irréversiblement. On indique la dispersion et la formation de LSC de base.

ADMIXTURE, TRICALCIUM-SILICATE, HYDRATION, LIGNOSULFONATE

Introduction

Lignosulfonic acid and its salts are widely used as water-reducing and set-retarding admixtures in concrete practice. These admixtures are known to extend the setting time by 30 - 60%, reduce the water requirement from 5 - 10% and increase the compressive strength at 28 days by 10 - 20%.

Even small amounts of lignosulfonate influence considerably the physical-mechanical properties of concrete and hence it is generally believed that the mechanism of the action of the admixture involves the phenomenon of adsorption. Attempts have been made to study the adsorption of admixtures on portland cement and the individual cement minerals such as C_3S, C_2S, C_3A and C_4AF* (1-9). In most studies the amount of the admixture adsorbed by the cement minerals was determined by exposure to an aqueous solution. By this method hydration of the adsorbent could not be avoided, and consequently conclusions drawn from such experiments are questionable.

In a hydrating cement, at any stage of hydration, both the unhydrated and hydrated phases co-exist, and the presence of an admixture such as calcium lignosulfonate (CLS) may result in interactions with these two types of phases. In view of this it was thought that a more realistic approach to the study of adsorption isotherms should involve (a) measurements under conditions in which the cement mineral does not hydrate. This condition may be achieved by using a non-aqueous solvent for CLS. (b) Determination of the adsorption isotherm on the hydrated phases using both aqueous and non-aqueous media. Attempts to explain the action of CLS on C_3S should include studies on the C-S-H and CH phases. (c) Study of the desorption scanning branches emanating at different points on the main adsorption curve. This should indicate the type of surface interaction. By adopting the above approach, some success has been achieved in an understanding of the influence of CLS on C_3A and its hydration products (10, 11).

Prior studies in this Division were concerned with the effect of CLS on the microstructure and morphology of Portland cement and its constit-

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*Notations used in this paper: C = CaO, S = SiO_2, A = Al_2O_3, F = Fe_2O_3, H = H_2O, CLS = Calcium lignosulfonate, H-C_3S = bottle-hydrated C_3S.

uents (12). This paper examines the adsorption of CLS on C_3S, CH and H-C_3S with the hope of revealing the mechanism of the action of this admixture.

Materials and Procedure

Materials

Tricalcium silicate used in this work contained 99.33% C_3S, 0.21% C_3A and 0.46% free lime and had a Blaine surface area of 3310 sq cm/g.

Details of the preparation and characterization of the C_3A phase and its hydrates are given in another publication (10).

Calcium hydroxide was obtained by a calcination of $Ca(OH)_2$ (analar) at 1000°C for 5 hours to decompose the $CaCO_3$ that may have been a contaminant. The resultant CaO was hydrated in an excess of double distilled water. The excess water was removed by vacuum drying.

The bottle-hydrated C_3S (H-C_3S) was prepared by hydrating C_3S over a rotating wheel for 1-1/2 years at a water/C_3S ratio of 5. After filtration the material was dried at 11% R.H. over a saturated solution of $LiCl.H_2O$. This material did not show any lines for C_3S in the X-ray pattern.

Calcium lignosulfonate (CLS) in the form of powder was supplied by Lignosol Ltd., Quebec. This material was obtained by chemically treating the spent liquor to destroy sugars. The sample contained 4.5% reducing bodies, mainly as reducing end groups tied to the lignosulfonate molecule.

Methods

Differential thermal analysis (DTA) was carried out in air or in a flow of N_2 using a DuPont-900 Thermal Analyser. Surface area was obtained using N_2 as the adsorbate by a Numinco-Orr surface area-pore volume analyser. The pH values were determined by the standard Beckman pH meter. Free lime in the H-C_3S sample was estimated by the well-known solvent variation method (13).

The conduction calorimeter containing six chambers was supplied by Institute of Applied Physics, Delft. Though the chambers are coated with teflon, the hydrated products tended to stick to the surface; therefore, use of polyethylene liners was necessary. The sensitivity of the calorimeter is 40 mV/W.

A Perkin-Elmer double-beam 350 spectrophotometer was used to estimate CLS in solutions.

Procedure

Adsorption-desorption isotherms were determined on C_3S, H-C_3S or CH by exposing them to different concentrations of CLS in an aqueous medium or in dimethyl sulfoxide.

To 0.5-g samples, each contained in different stoppered polypropylene tubes, were added 15 cc of the CLS solution of concentrations ranging from 0.015 to 1.0%. The tubes were rotated continuously for a day. At the end of this period the suspension was centrifuged and 10 cc of the supernatant solution withdrawn, dilute HCl added to obtain a pH of 3.0 and the concentration of CLS estimated by the spectrophotometric method at a wavelength of 375 mμ. The difference in the amount of CLS added originally and that left in the solution gave the percentage of CLS adsorbed by the solid. At higher concentrations of CLS the solutions were adequately diluted for spectrophotometric determination.

Scanning curves on the desorption branch were obtained as follows. At any point on the adsorption curve, after pipetting out 10 cc of the supernatant solutions for CLS determination, 10 cc of distilled water or dimethyl sulfoxide was added to the mixture. The tube was then rotated on rollers for 2 - 3 days. At the end of this period the concentration of CLS and the amount of CLS held by the solid were determined as before. The same procedure was adopted to obtain the second point on the desorption branch.

Results

In the determination of the amount of CLS sorbed by C_3S in an aqueous medium, the ordinate refers to the initial concentration of CLS, rather than the equilibrium concentration because C_3S, especially at low CLS concentrations, is not stable. It should also be stated that each of the points was obtained through a separate run. In the C_3S-CLS-H_2O system at low concentrations of CLS there is a steep increase in the amount of adsorption up to a concentration of about 0.1% CLS (Fig. 1). Above this concentration a steep drop in the amount of adsorption is noticeable. At concentrations above about 0.15% there is a gradual increase in the amount of adsorption. On the desorption branch starting from 4 points at low concentration levels (situated on the steep portion of the adsorption curve) there is almost complete irreversibility of adsorption (Fig. 2). Desorption from points corresponding to initial concentrations of 0.5, 0.7 and 1.0% CLS show a different trend (Fig. 1). Some irreversibility in the amount of adsorption is evident to concentration levels of about 0.15 - 0.2%, but below these values there is a steep and significant increase in the amount of adsorption.

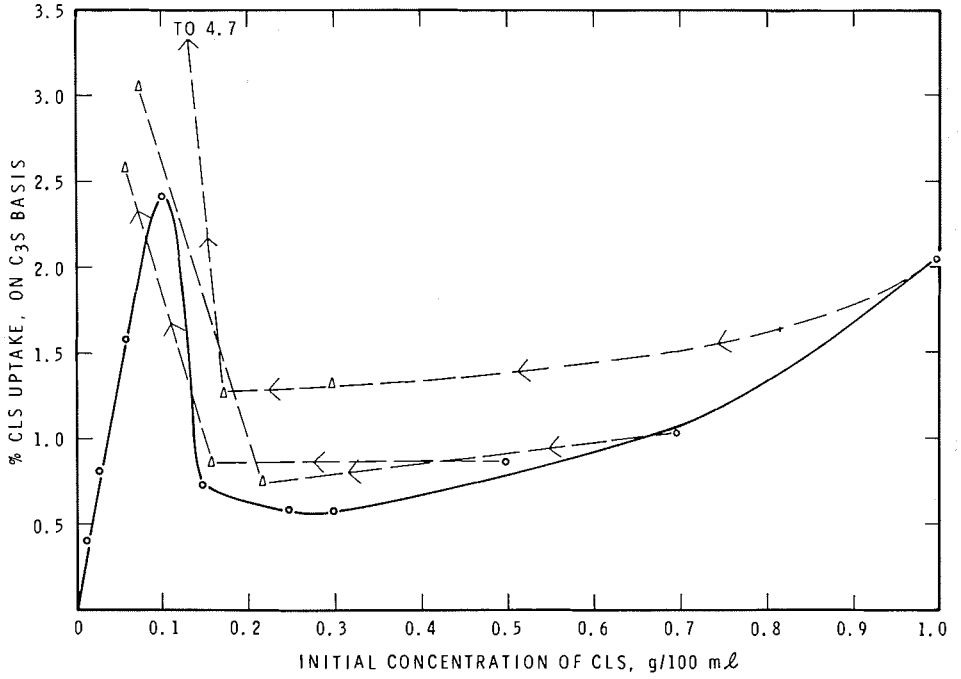

FIG. 1

Adsorption of calcium lignosulfonate on C_3S in an aqueous medium.

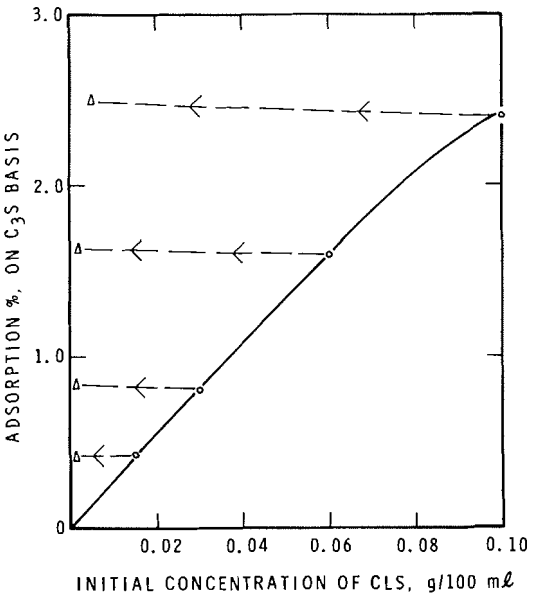

FIG. 2

Adsorption-desorption curves of CLS on C_3S in an aqueous medium at low CLS concentrations.

Figures 3 and 4 refer to the adsorption-desorption isotherms of CLS on the H-C_3S sample using water and dimethyl sulfoxide respectively as solvents. The equilibrium concentrations are plotted on the abscissa, as the adsorbent is stable. Each point on the adsorption curve refers to a separate run. In the aqueous medium there is a rapid initial adsorption of CLS followed by a much slower rate at higher concentrations. The scanning desorption isotherms do not follow the adsorption isotherm. A similar trend is evident in the isotherms using dimethyl sulfoxide as the solvent, but at any equilibrium concentration more CLS is adsorbed by the H-C_3S sample in an aqueous medium.

The adsorption-desorption isotherms of CLS on the CH phase are shown in Fig. 5. The amount of adsorption increases with the concentration but the rate gradually decreases. The scanning isotherms show almost complete irreversibility at low concentrations studied.

Discussion

Interaction of CLS with C_3S in H_2O

The C_3S phase adsorbs practically no CLS in a non-aqueous medium. This is expected, considering the low surface area of C_3S available for the adsorbate. In an aqueous medium, however, sorption seems to occur. In

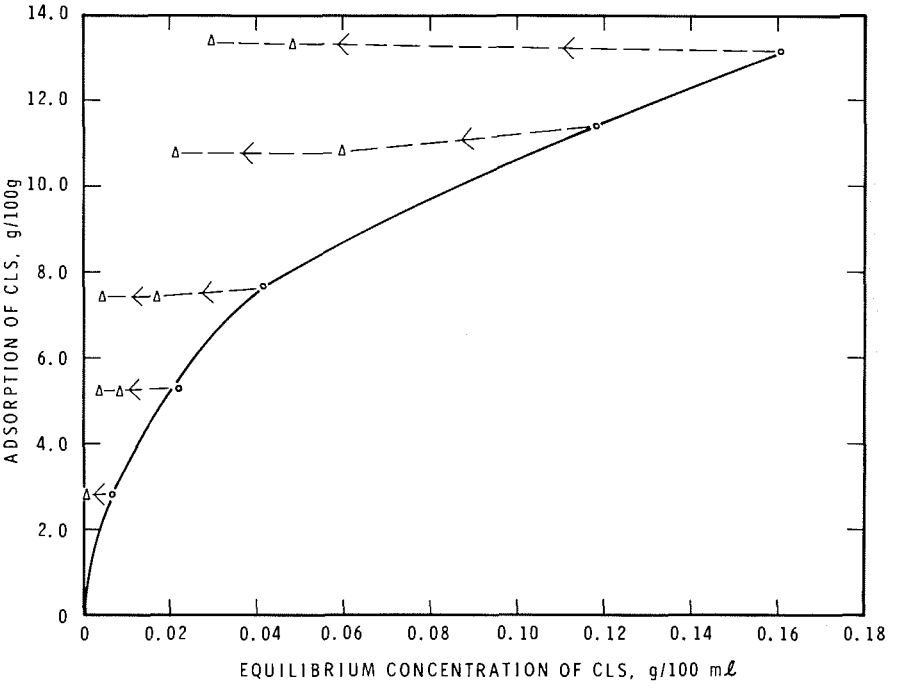

FIG. 3

Adsorption-desorption isotherms of CLS on hydrated C_3S in the aqueous medium.

FIG. 4

Adsorption-desortpion isotherms of calcium lignosulfonate on the hydrated C_3S in a non-aqueous medium.

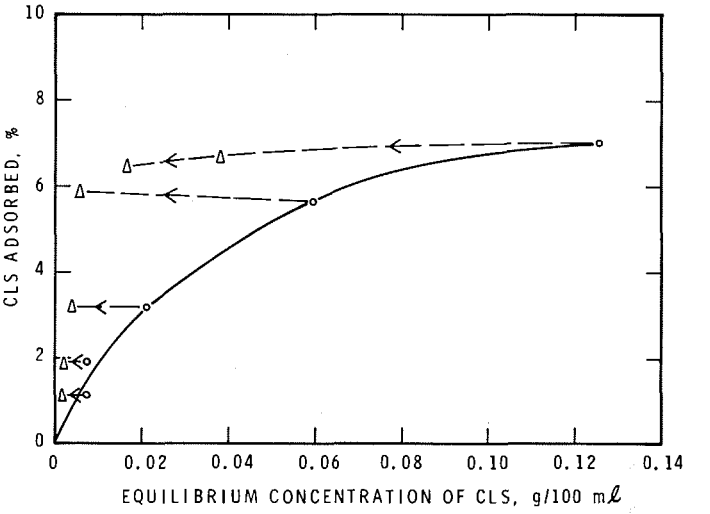

Fig. 1 the adsorption-desorption characteristics may be explained as follows. The initial steep portion indicating adsorption of increasing amounts of CLS is due to the formation of a high surface area, hydrated C_3S (N_2 surface area ~70 m^2/g). The hydration of C_3S is facilitated in the presence of low CLS concentrations. At a CLS concentration of about 0.15% CLS there is a decrease in the adsorption value. At a concentration

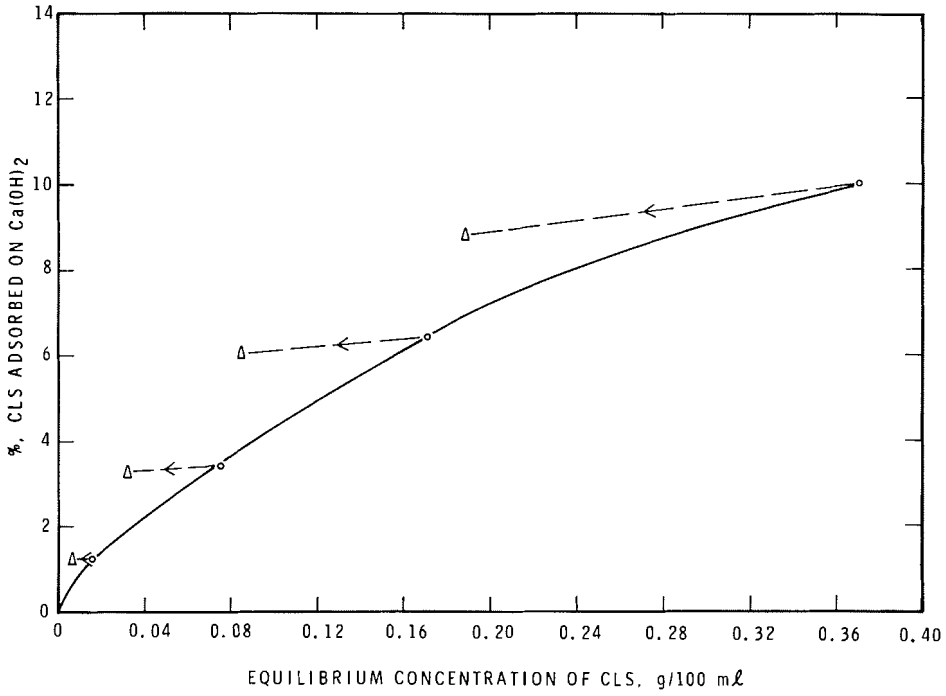

FIG. 5

Adsorption-desorption isotherms of CLS on $Ca(OH)_2$.

of 0.3% and beyond, the hydration of C_3S seems to be practically nil. The gradual increase in the adsorption value for initial concentration levels from 0.3 to 1.0% CLS may be due to the dispersion of C_3S particles. The dispersion increases the surface available for the CLS molecules. In addition, multimolecular adsorption of CLS may result. The dispersion of cement particles is known to occur and increase as the concentration of CLS is increased (1).

The above explanation is in accord with the DTA data (Fig. 6). The curve A corresponding to the sample on the peak of the adsorption curve shows a broad endothermal effect below 250°C and a sharp endothermic effect between 450°C and 500°C. The two inflections are respectively due to the dehydration of C-S-H and $Ca(OH)_2$ in the hydrated C_3S product. The exothermal effect at about 300°C is due to the oxidation of CLS. This is absent in an atmosphere of N_2. The points B and C, representing points of low CLS adsorption, fail to indicate peaks for the presence of hydrated C_3S. Thermograms show that the intensity of the exothermic peak is greater for

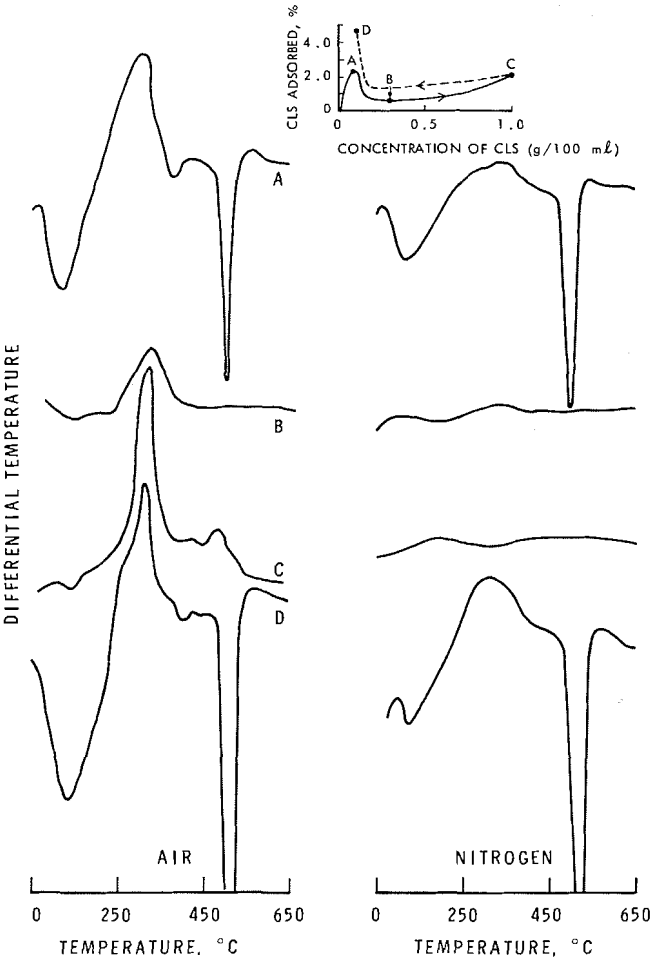

FIG. 6

Thermograms of C_3S treated with CLS in an aqueous medium. (Curves A, B, C, D correspond to the samples taken at different points on the adsorption-desorption curve drawn above.)

samples containing more adsorbed CLS. The pH value of the solution corresponding to the point A is much higher than those corresponding to points B and C confirming that there is practically no hydration at concentration levels represented by points B and C.

The irreversibility in the desorption branches at concentrations up to about 0.1% should indicate that CLS is strongly adsorbed on the hydrated C_3S as a complex (Fig. 2). It appears that in the system C_3S-CLS-H_2O it has wrongly been assumed that adsorption occurs only on the C_3S surface, even at low CLS concentrations.

The scanning desorption branches from different points beyond a concentration of 0.5, 0.7 and 1% CLS may be explained as follows. The partial irreversibility up to a concentration of about 0.15 - 0.25% CLS on the desorption branch may possibly represent the existence of a strongly

bound surface complex involving the ions on the surface of C_3S, CLS and H_2O. The steep increase in the adsorption values at concentrations less than about 0.25% CLS is due to the formation of the hydrated C_3S product, which is facilitated at low CLS concentrations. The formation of hydrated C_3S at these concentrations is confirmed from the thermogram (curve D, Fig. 6). The thermogram shows large endothermic peaks representing the presence of C-S-H and CH. On the desorption branch the amount of CLS adsorbed is significantly more for sample C than for the others because it must have dispersed and consequently hydrated to a greater extent (Fig. 1).

The inhibitive effect of CLS on the hydration of C_3S does not seem to be a simple function of the percentage of its presence with respect to C_3S. The concentration in the aqueous phase and the water/solid ratio are other factors to be taken into account. In Fig. 7 curves A, B, C and D represent the conduction calorimetric curves for C_3S treated respectively with 0%, 0.125%, 0.25% and 1% solution of CLS at a water/solid ratio of 2. If C_3S is treated with 1% CLS solution at a water/solid ratio of 0.5, the percentage of CLS on the basis of C_3S would be 0.5, the same as sample C. The resulting curve would, however, be similar to D. All the above results seem to suggest that C_3S is stabilized in contact with a CLS solution of concentration above about 0.25%.

The influence of the CLS concentration on the inhibitive action on the hydration of C_3S may be illustrated with another example. In the hydration of C_3S the inhibitive action of CLS may be countered by the addition of small

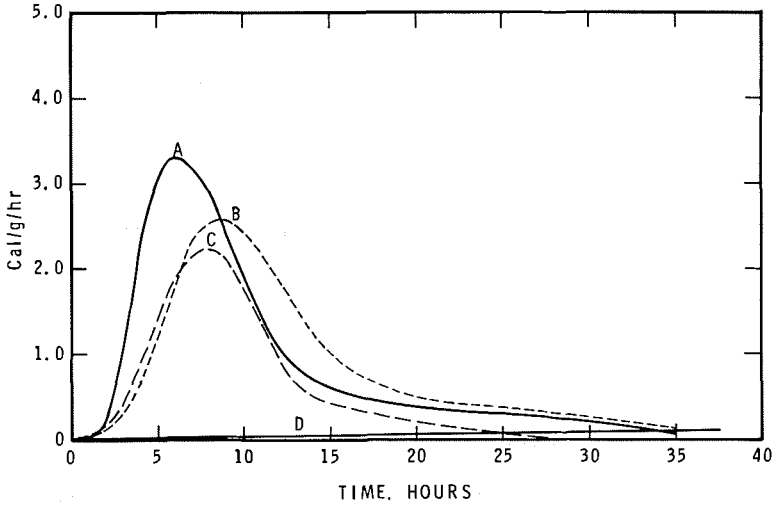

FIG. 7

Rate of hydration of C_3S as a function of the concentration of CLS by conduction calorimetry.

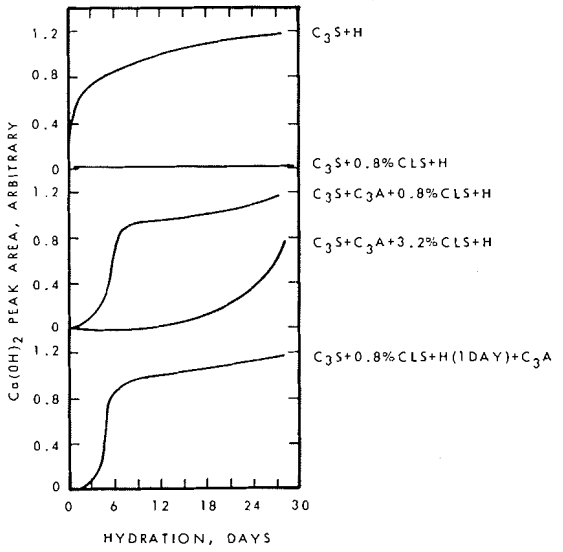

FIG. 8

Influence of CLS on the hydration of C_3S in presence of C_3A.

amounts of C_3A or its metastable hydrates. The C_3A phase consumes large amounts of CLS, leaving the solution dilute with respect to CLS. By the addition of 0.8% CLS (on C_3S basis) the hydration of C_3S is stopped almost indefinitely (Fig. 8). By mixing 5% C_3A with C_3S, hydration of C_3S proceeds normally after three days. This indicates that by interaction of CLS and C_3A the solution attains a low CLS concentration, facilitating desorption of the surface complex on the C_3S phase. By starting with a CLS concentration of 3.2%, the inhibitive action may be prolonged (curve 4, Fig. 8). A C_3S sample, pretreated with a solution of CLS for a few minutes, dried and subsequently exposed to the action of C_3A requires 3 days before the inhibitive action of CLS is removed. This indicates that CLS forming a surface complex on the C_3S phase in an aqueous medium is not easily desorbed. The formation of this complex occurring as soon as CLS solution comes into contact with C_3S may be compared to the formation of a surface hydrated product of C_3S with water in the induction period. Just as the induction period is reduced at the higher water/solid ratio, the inhibitive action of the complex formed with CLS is also reduced with an increase in the water/CLS ratio.

Interaction of CLS with Hydrated C_3S in Aqueous or Non-aqueous media

The adsorption-desorption isotherms of CLS on the hydrated C_3S (H-C_3S) are shown in Figs. 3 and 4. The scanning isotherms do not follow

the adsorption, showing increasing amounts of irreversibility of the adsorbed CLS as the concentration increases.

At any equilibrium concentration the adsorption values are much greater in the aqueous than in the non-aqueous medium. Water molecules seem to disperse the hydrated C_3S better and to promote penetration of CLS into the layer positions of the C-S-H phase. In the C_3S-CLS-H_2O system an increasing amount of adsorption at higher concentrations was attributed to the dispersion effect. In order to test whether this is likely to occur in the H-C_3S samples, N_2 surface areas were determined for samples containing 0, 2.8, 7.7 and 13.2% adsorbed CLS. Neglecting the surface area of adsorbed CLS (0.69 m^2/g) the recalculated values of surface area of the H-C_3S component of the above samples are 66.0, 67.9, 71.2 and 67.9 m^2/g. The differences between values are not significant enough to suggest dispersion.

The results indicate that CLS not only adsorbs as a surface complex on the H-C_3S phase but also enters the interlayers of the C-S-H phase. This was also observed for the hexagonal calcium aluminate phase in which the interlayer penetration was attended by an increase in the c-axis. It is not possible to check this for the C-S-H phase because of the difficulty of obtaining diffraction lines corresponding to the c-spacing. The entry of CLS into the interlayers of C-S-H need not necessarily result in an increase in the N_2 surface area because in samples that are predried prior to surface area determination the entrance of the interlayers is sealed (14). It is possible that the penetration of CLS may have a bearing on the shrinkage and creep characteristics of cement containing the CLS admixture. Under the conditions of low CLS concentrations and very short periods allowed for equilibration by previous workers, CLS may be bound mainly as a surface complex and not enter the interlayer positions in the C-S-H phase (8).

The thermograms of H-C_3S treated with CLS, in addition to showing exothermic peaks for the oxidation effects in the CLS, also exhibit the typical large endothermal effect at about 800°C due to the CLS-HC_3S complex (Fig. 9). The curve D, representing the sample containing 13.2% CLS, shows an exothermal effect at about 700°C followed by a large

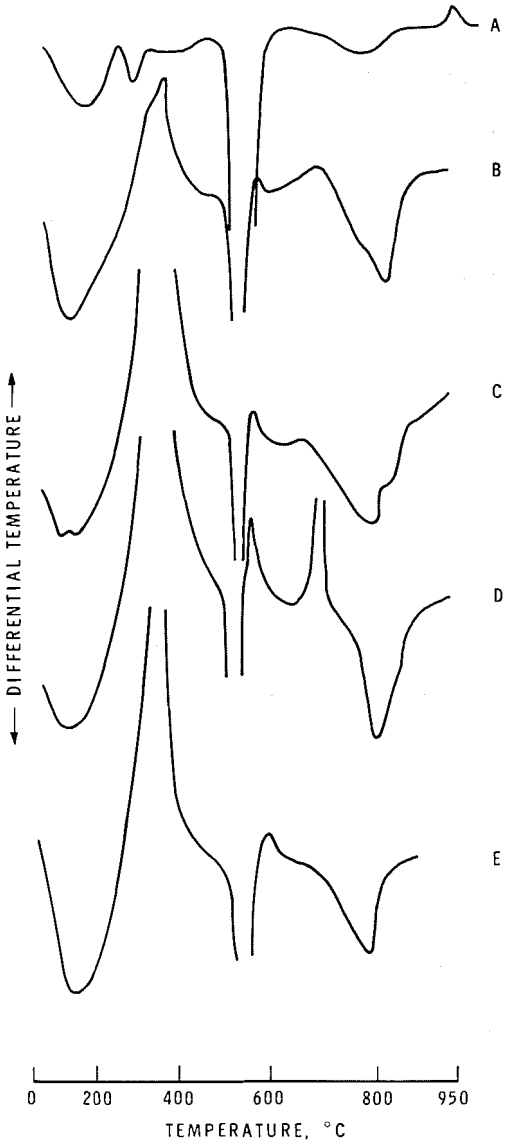

FIG. 9

Differential thermal curves of hydrated C_3S with different amounts of adsorbed CLS.
A = H-C_3S + 0% CLS;
B = H-C_3S + 2.8% CLS;
C = H-C_3S + 7.7% CLS:
D = H-C_3S + 13.2% CLS;
E = H-C_3S + 7% CLS (Non-aqueous medium).

endothermal effect at 800°C. This is similar to the thermal curve for the hexagonal aluminate hydrate containing CLS in the interlayer spaces (11).

Interaction of CLS with Calcium Hydroxide

The amount of CLS adsorbed by CH increased with the concentration of CLS (Fig. 5). The increase in adsorption with concentration may be due to the dispersion of the $Ca(OH)_2$ particles and an increase both in the physical and chemical interactions of CLS with CH. The surface area of CH is 16.2 m^2/g and that containing about 10% CLS shows an increased area of 22.6 m^2/g. In the hydrated C_3S the contribution to the surface area

due to the dispersion of CH is difficult to assess. The hydrated C_3S containing about 35% CH has a total surface area of about 66 m^2/g. In addition to its presence in smaller proportions, the surface area of CH is less than that of the C-S-H component. In the H-C_3S sample containing CLS the small increase in the surface area may be attributed to the dispersion of the CH phase.

The desorption isotherms show large irreversibility at all concentrations (Fig. 5). The small amounts of reversibility at higher concentrations may indicate a physical adsorption effect. The irreversible nature of the scanning desorption isotherm suggests a chemical interaction between CLS and CH. At high lime concentrations the CLS forms an insoluble basic lignosulfonate.

Thermograms of CH containing 1.2%, 3.4%, 6.4% and 10.0% CLS show clearly an exothermic effect at about 300°C due to oxidation of CLS (Fig. 10). There is also an endothermal effect at about 750 - 800°C

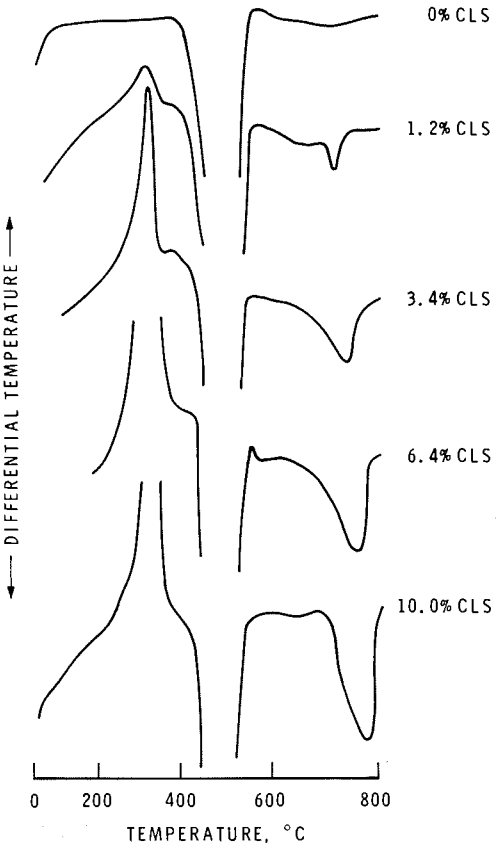

FIG. 10

Thermograms of $Ca(OH)_2$ containing different amounts of adsorbed CLS.

representing the presence of the basic CLS. The intensity of this effect progressively increases with the amount of the irreversible CLS. The temperature of the endothermal effect, and its increased intensity with the CLS content, reveal that it is not due to the presence of $CaCO_3$.

Conclusions

At low concentrations of CLS in the tricalcium silicate-calcium lignosulfonate-water system, it is the hydrated C_3S and not C_3S that is responsible for perceptible amounts of adsorption. There is practically no adsorption of CLS on the C_3S phase in a non-aqueous medium. Higher concentrations of CLS, in addition to inhibiting the hydration of C_3S, seem to disperse it. The retarding or inhibiting influence of CLS is mainly dependent on its concentration in solutions and not on its proportion with respect to C_3S. The action of CLS on the hydration of C_3S at early periods is related to the stability of the surface complex involving the silicate surface, CLS and H_2O. The surface complex is less stable as the CLS/H_2O ratio decreases. Both C-S-H and CH phases irreversibly adsorb CLS. There is an indication that CLS not only chemisorbs on the C-S-H surface but also enters the interlayer positions.

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