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EFFECT OF CALCIUM LIGNOSULFONATE ON TRICALCIUM
ALUMINATE AND ITS HYDRATION PRODUCTS

BY

V. S. RAMACHANDRAN AND R. F. FELDMAN

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L'EFFET DU LIGNOSULFONATE DE CALCIUM SUR L'ALUMINATE
DE TRICALCIUM ET SES PRODUITS D'HYDRATATION

SOMMAIRE

On a trouvé, dans le système aluminat de tricalcium - lignosulfonate de calcium - eau, l'évidence de la formation d'un complexe et de la précipitation d'un lignosulfonate très basique. L'hydrate d'aluminat de calcium hexagonal et l'hydrate d'aluminat cubique adsorbent irréversiblement le lignosulfonate de calcium. Les résultats de l'adsorption sont des changements d'aire superficielle, de morphologie, de comportement thermique et d'interconversions.

Effect of calcium lignosulfonate on tricalcium aluminate and its hydration products ⁽¹⁾

V.S. RAMACHANDRAN ⁽²⁾, R.F. FELDMAN ⁽³⁾

In the tricalcium aluminate - calcium lignosulfonate - water system, evidence has been obtained for the formation of a complex and precipitation of a highly basic calcium lignosulfonate. The hexagonal calcium aluminate hydrate as well as the cubic aluminate hydrate irreversibly adsorb calcium lignosulfonate. Adsorption results in changes of surface area, morphology, thermal behaviour and rate of interconversions.

INTRODUCTION

In concrete practice water-reducing and set-retarding admixtures are extensively used because they are known to confer certain beneficial effects. These admixtures are usually based on lignosulfonic acids and their salts or on hydroxylated carboxylic acids and their salts, the former being more common. In spite of extensive work on the role of these admixtures on the physical-mechanical behaviour of concrete, the exact mechanism of their action is not clear.

A direct study of the influence of calcium lignosulfonate (CLS) on the hydration of cement, though a useful approach from the practical point of view, is not easy to interpret because of the mutual influences of the individual cement compounds such as tricalcium silicate (C_3S) ⁽⁴⁾, C_2S , C_4AF , C_3A , alkalis and gypsum. In many instances it has been very useful to study first the single, binary and ternary systems

before extending the study to the cement itself. These results are shown to be of value in interpreting the behaviour of cement in terms of its components.

Much work has been done on the influence of CLS on the hydration behaviour of the C_3A phase. It has been concluded that lignosulfonate has a stabilizing effect on the metastable hexagonal phases of the aluminate hydrate with respect to the cubic calcium aluminate hydrate [1-8].

Application of techniques such as X-ray, differential and thermogravimetric analysis, conduction calorimetry and electron microscopy has yielded useful results on the role of lignosulfonate in the hydration behaviour of C_3A . As the amount of calcium lignosulfonate required to retard the hydration of cement is very small, several investigators have attempted to explain the mechanism of its retarding action through a study of the adsorption of CLS on anhydrous cement compounds [9-18]. In these studies the applicability of the terms "adsorption", "equilibrium" and "adsorbent" may be somewhat questionable. In studies concerning the adsorption of CLS on C_3A the total amount of CLS taken up by the solid is often referred to as the amount of CLS adsorbed by the C_3A . It is known, however, that C_3A hydrates to C_4AH_n , C_2AH_n and C_3AH_6 , depending on the concentration of CLS and the duration of contact with H_2O . In addition, the morphology of the hydrated calcium aluminate hydrate may change in the presence of CLS. Reh binder and coworkers observed an acicular crystal formation whereas others obtained hexagonal plates as the initial hydration product of C_3A in the presence of CLS [1-6].

It is thought that a more realistic approach might be to study the adsorption of CLS on the hydrates of tricalcium aluminate under conditions that eliminate interconversions. In concrete practice a dosage of 0.8 per cent CLS approximates 8 per cent CLS with

⁽¹⁾ The information in this paper was presented at the Second Cement Symposium held as part of the 73rd Annual Meeting of the American Ceramic Society, Chicago, April 1971.

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⁽⁴⁾ The standard notation generally used in cement chemistry is adopted here: C = CaO , S = SiO_2 , A = Al_2O_3 , F = Fe_2O_3 and H = H_2O . (Calcium lignosulfonate is abbreviated to CLS.)

respect to the C_3A phase. Most of this admixture seems to be used up by the calcium aluminate and its hydrates. In the present work the amount of CLS with respect to C_3A or the hexagonal phases is deliberately kept between about 6.0 and 200 per cent to enable determination of the adsorption isotherm and to accentuate the complex effects. Such a method is very commonly applied in cement chemistry. The results thus obtained can be extrapolated to explain the actual effects of the admixture used in small quantities in practice.

In the first part of the investigation adsorption of CLS was studied in a non-aqueous medium using dimethyl sulfoxide. The results indicated that C_3A and C_3AH_6 adsorb little if any CLS, whereas the hexagonal phase containing C_4AH_n and C_2AH_n together adsorbs about 2.2 per cent CLS [19].

This paper attempts to discuss the significance of the adsorption of CLS on the C_3A , $C_4AH_n - C_2AH_n$ and C_3AH_6 phases in an aqueous medium. For the hexagonal phase the mixture $C_4AH_n - C_2AH_n$ rather than individual hydrates was chosen because the mixtures are formed together in the hydration of C_3A [4, 20-25]. For correlation, the samples, treated with CLS where necessary, were also subjected to a study by techniques involving surface area, thermogravimetric analysis, differential thermal analysis, X-ray diffraction, chemical analysis and electron microscopic examination.

EXPERIMENTAL

Materials

Tricalcium aluminate of high purity was supplied by the Portland Cement Association, U.S.A. The powder had a Blaine surface area of 4350 sq cm per g. The hexagonal calcium aluminate hydrates comprising C_4AH_n and C_2AH_n (referred to as the hexagonal phase) were prepared by hydration of C_3A at 2 °C for 5 days. The cubic calcium aluminate hydrate C_3AH_6 (referred to as the cubic phase) was prepared by steam-curing C_3A at a pressure of 100 lb/sq in. for 24 hours.

Calcium lignosulfonate (CLS) sample in the form of powder was supplied by Lignosol Chemicals Ltd., Quebec. This material was obtained by chemically treating the spent sulfite liquor to destroy sugars. The sample had 4.5 per cent reducing bodies, mainly as reducing end groups tied to the lignosulfonate molecules. Nearly 90 per cent of the CLS had a molecular weight in the range 4000 to 8000.

Details of the preparation of the materials and their characterization by X-ray, differential thermal, thermogravimetric, chemical, infrared and electron microscopic analysis are reported elsewhere [19].

Method

A brief description of the techniques used in this work follows :

CLS in solutions was estimated by a Perkin-Elmer double-beam 350 spectrophotometer.

Differential thermal analysis (DTA) was carried out in air or in a flow of N_2 using a Du Pont 900 thermal analyser.

Fig. 1. — Calibration curves for calcium lignosulfonate at different pH values.

Thermogravimetric analysis (TGA) was carried out in vacuum using a sensitive Cahn balance.

Surface area was determined with nitrogen as the adsorbate by a Numinco Orr surface area-pore volume analyser.

X-ray diffractograms were obtained by a Hilger and Watts unit using CuK_{α} source.

Electron microscopic examination was carried out by both scanning and transmission methods using Cambridge Stereoscan Mark 2A and Philips EM-75 instruments, respectively.

Calcium and aluminium in some of the samples were estimated by Perkin-Elmer 403 atomic absorption spectrophotometer.

pH values were determined by the standard Beckman pH meter.

Determination of the Isotherm

A series of preliminary experiments was carried out using different solid/solution ratios and concentrations of CLS to determine the minimum concentration of CLS at which the hexagonal phase does not convert to the cubic phase. Adsorption-desorption isotherms on the hexagonal phase were obtained as follows. To 0.5 g samples of the hexagonal phase, each contained in seven different stoppered polypropylene tubes, were added 30 cc of aqueous solution of CLS of concentrations varying from 0.12 to 0.89 g/100 ml. The tubes were rotated continuously for 24 hours. Preliminary experiments on the rate of adsorption showed that this period was more than adequate for equilibration. At the end of 24 hours the suspension was centrifuged and 10 cc of the clear supernatant solution was 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 m μ . The concentration of unadsorbed CLS thus obtained is referred to as equilibrium concent-

Fig. 2. — Electron micrographs in the C_3A -CLS- H_2O system.
a) Calcium lignosulfonate ($\times 600$),
b) Tricalcium aluminate ($\times 6500$),
c) Dark brown gel ($\times 7000$),
d) Product formed in the C_3A -CLS (30 %) - H_2O system ($\times 2800$),
e) Same as d ($\times 7000$),
f) Same as d ($\times 14,000$).

ration. The difference in the amount of CLS added originally and that left in the solution after adsorption gave the percentage of CLS adsorbed by the solid. At higher CLS concentrations the solutions were diluted with water for spectrophotometric determination. All the experiments were conducted at a temperature of $21 \pm 1^\circ C$.

Points on the desorption branch were obtained as follows : After determining the amount of adsorption at a particular equilibrium concentration, a further 10 cc of the supernatant solution was withdrawn. Thus, a total of 20 cc was withdrawn from 30 cc of the solution. This volume was replenished by the addition of 20 cc of distilled water, mixed and, as before, rotated over the rollers for about 3 days. At the end of this period the concentration of CLS was determined at a pH of 3.0 and the amount of CLS held by the solid calculated. Up to three points were obtained on the desorption branch for each point on the adsorption curve.

Adsorption-desorption isotherms were obtained for the cubic phase, as explained, but at initial concentrations ranging from 0.025 to 0.20 g/100 ml.

TABLE I. — Various phases formed in the C_3A -CLS- H_2O system

Starting Material	Phases Observed at Different Periods			
	6 hours	3 days	7 days	6 months
$C_3A + H_2O$	C_3A C_2AH_8 C_4AH_{13}	C_3A C_2AH_8 C_4AH_{13} C_3AH_6	C_3A C_3AH_6	C_3AH_6
C_3A -CLS- H_2O	C_3A C_2AH_8 C_4AH_{13}	C_3A C_2AH_8 C_4AH_{13}	C_3A C_2AH_8 C_4AH_{13}	C_3AH_6

RESULTS AND DISCUSSION

Estimation of Calcium Lignosulfonate

An accurate estimation of CLS is essential if meaningful conclusions are to be drawn in any work on the adsorption of CLS on cementitious components. The spectrophotometric method is commonly used to estimate CLS in an aqueous solution. Estimated values are dependent on the pH values of the CLS solution. Non-recognition of this fact and lack of details on the actual conditions of estimation in the literature make comparison of results difficult. In some instances it may explain the divergence of values reported for a particular material.

Figure 1 shows calibration curves for the estimation of CLS under controlled pH values of 3.0, 6.0 and 12.0, and one without control. All have different slopes. An aqueous solution of lignosol having a pH of 6.5 to 7.0 when brought into contact with C_3A will have a pH of about 11.5 to 12.0. If the calibration curve obtained at pH 6.5 to 7.0 is used for the estimation of unadsorbed CLS in the C_3A -CLS- H_2O system the values will be very different, as may be inferred from the slopes of the lines at different pH conditions. It is essential that determinations should be carried out at a constant pH. At pH 3.0 and below it has been observed [9] that CLS can be determined more accurately and that the CLS solution does not exhibit any turbidity. In the present work, therefore, CLS was estimated at a constant pH of 3.0. The suggestion that hydration should be carried out at a constant pH in a buffer medium may be unacceptable because the addition of extraneous cations and anions, by themselves, may influence the kinetics of hydration.

Tricalcium Aluminate - Calcium Lignosulfonate - Water System

The retardation effect of CLS in portland cement is mainly attributed to large adsorption effects of CLS on the C_3A phase. This conclusion is based on results obtained when portland cement and its components are treated with CLS in an aqueous medium. The adsorption values are reported to be in the order $C_3A > C_4AF > \text{portland cement} > C_3S > C_2S$. This cannot be explained on the basis of surface areas of the components, 0.16, 0.11, 0.55 and 0.53 m^2/g , respectively, for C_3A , C_4AF , portland cement and C_3S [12].

In adsorption experiments on the C_3A phase the solid is kept in contact with an aqueous solution of CLS. The data are incorrectly referred to as the amount of adsorption of CLS on C_3A . The uncertainty of the composition of the adsorbent can be illustrated by the following example in which one gram of C_3A is treated with 1.00 cc of an aqueous solution containing 0.5 per cent CLS.

Table I shows that, in the presence of CLS, C_3A converts to hexagonal and cubic hydrates more slowly; the degree of hydration depends on the concentration of CLS, the time of contact, temperature, etc. It has been reported that, other conditions being equal, the amount of adsorption of CLS on cement is dependent only on the amount of CLS and not on its concentration in H_2O [9, 15]. All this suggests the complicated factors involved in the determination of adsorption in a system containing C_3A -CLS- H_2O . In the literature the reported adsorption values of CLS on C_3A in an aqueous environment show a large variation between 15 and 450 per cent [12, 16, 26].

The significance of the so-called adsorption of CLS on C_3A was examined by studying the effect of different concentrations of aqueous solutions of CLS : 15, 30, 50, 100 and 200 per cent. At concentrations equivalent to 50 per cent CLS and above, a large amount

Fig. 3. — Thermograms of products formed in the C_3A -CLS- H_2O system.

Fig. 4. — Thermograms of products in the hexagonal phase - CLS- H_2O system.

of a gelatinous type of dark brown floc (herein referred to as gel) settled on a heavier light brown mass probably including the original material (referred to as light brown). Neither was apparent at concentrations of 30 per cent CLS or less, but, as the concentration of CLS increased, the demarcation between the gel and the light brown mass became more evident. Two portions were separated and subjected to further analysis. It should be noted, however, that it was not possible to prevent contamination of one with the other.

Dark brown gel

Electron microscopic examination revealed the gel as a fluffy mass typical of a non-crystalline material. It is different from C_3A , which shows as an irregular platy mass. The gel does not resemble calcium lignosulfonate, as may be seen in Figure 2. It is similar to CLS in not indicating any peaks in an X-ray diffractogram.

The surface area, as measured by N_2 adsorption, is only $0.85 \text{ m}^2/\text{g}$. This value is slightly higher than that of calcium lignosulfonate, with a value of $0.69 \text{ m}^2/\text{g}$, and of the pure C_3A with a value of $0.70 \text{ m}^2/\text{g}$. The gel is very slightly soluble in water. The starting material, i.e. CLS, is very soluble in H_2O . The gel contains 5.4 per cent Al and 14.3 per cent Ca, whereas CLS contains 7.0 per cent Ca and practically no Al.

The DTA curve of the gel is not similar to that of CLS, as may be seen in Figures 3 and 4. The intense

Fig. 5. — Comparative losses in weight for the gel and CLS at different temperatures.

exothermic peak at about 360 °C is common to both and is reduced to a small hump in vacuum DTA. The important difference is a large endothermal effect, with a peak at about 100 °C, and an exothermic peak at about 730 °C, which is not noticeable for the thermogram of CLS carried out in air (Fig. 4).

The vacuum TGA curve also is different from that of CLS. In Figure 5 a plot of the weight loss curve of the gel is compared with that of CLS for the same temperature. The resultant curve does not lie on the ideal curve of direct proportionality, showing thereby that the two materials are not exactly the same. At lower temperatures up to 200 °C the gel material loses more weight than does the CLS. Up to a temperature of about 450 °C the CLS loses more weight than the gel; beyond 450 °C the curve is steeper and the rate of loss for the gel material greater.

Light brown mass

The heavier light brown mass containing a small amount of whitish mass was separated from the gel, but some gel-like material remained as a contaminant. This portion had a surface area of 5.54 m²/g compared with that of the gel with a value of 0.85 m²/g and that of C₃A with a value of 0.70 m²/g. Differential thermogram of the light brown material containing white mass shows similar exothermal peaks as CLS-gel but much reduced intensities. The main difference was the emergence of an endothermal peak at about 870 °C (Fig. 3). In the X-ray diffractogram all the lines could be attributed to C₃A.

These results may be interpreted as follows : When C₃A is in contact with high concentrations of CLS, a dark brownish gel-like material forms and settles on the light brown mass. At a high CLS concentration and a high pH, a basic CLS is precipitated out that contains a higher calcium content than does CLS and includes some incorporated aluminium ions. Adding lime to CLS at a pH of 11.0 is known to form a basic calcium lignosulfonate insoluble in water [27,

28, 29] and should explain the very high apparent adsorption values reported by Reh binder et al [26] who must have used a high initial concentration of CLS.

It is unlikely that the gel formed at a high concentration of CLS is a compound of the formula C₃A.CLS.H_n analogous to the calcium sulfoaluminate, as reported by Hansen and Manabe et al [18, 30]. It is difficult to visualize how a large amount of CLS with very high molecular weight could form an isostructural compound with calcium sulfoaluminate. In addition, calcium lignosulfonate almost always has a range of molecular weights and invariably also contains impurities. If all Al in the dark brown gel is assumed to exist as C₃A in the complex C₃A.CLS.12H₂O, an approximate calculation (assuming the average molecular weight of CLS to be 6000) would show the molar proportions of C₃A : CLS to be about 1 : 0.08 instead of 1 : 1. If the complex of the formula C₃A.CLS.nH₂O has to form as the main product, it may require special conditions of initial proportions, starting material, ball-milling, etc.

The light-brown material contains mainly unhydrated C₃A (whitish) and a gel-like material, perhaps covering the C₃A particles. This gel-like material, as opposed to the dark brownish gel which forms in large quantities, has a higher surface area and shows some additional thermal effects (Fig. 3). This light-brown gel in the whitish mass resembles the behaviour of the hexagonal aluminate-CLS complex (described later).

In samples of C₃A treated with an aqueous solution of CLS containing 30 per cent CLS with respect to C₃A, the gel-like material could not be separated. The solid phase appeared as a light-brown mass showing a morphology different from that of the gel separated from the mixtures of C₃A-CLS-H₂O at high CLS concentrations (Fig. 2). It exhibited a honeycomb structure that, on closer examination, appeared to consist of twisted and curled ribbons. Some appeared

Fig. 6. — Adsorption-desorption isotherms of calcium lignosulfonate on the hexagonal phase.

as fluffy masses. X-ray examination showed lines that could only be ascribed to the presence of C_3A . The surface area was $16.2 \text{ m}^2/\text{g}$, being higher than that of C_3A , CLS, or the gel portion formed at high CLS concentrations in the C_3A -CLS- H_2O system. Differential thermograms of this product showed effects different from those for CLS, with two endothermal effects at about 100 and 840°C and an exothermic peak at about 820°C . In a nitrogen atmosphere the exothermal effects were suppressed and the thermogram revealed two endothermal effects below 300°C typical of the hexagonal phase.

In the presence of an aqueous solution of CLS (30 per cent with respect to C_3A) it appears that CLS reacts with C_3A to form a non-crystalline complex with high surface area. Possibly this is related to the complex of CLS with the hexagonal calcium aluminate hydrate. The thermal results for the product obtained with 50 per cent CLS equivalent show more clearly some of the effects for the complex (Fig. 3).

Hexagonal Aluminate - Calcium Lignosulfonate - Water System

Unlike the C_3A -CLS- H_2O system in which it is not possible to determine the adsorption isotherm, it is more convenient to study the adsorption isotherms of the hexagonal phase-CLS- H_2O system. To be meaningful, concentrations of CLS should be so chosen that the hexagonal phase is stable and does not convert to the cubic phase. It was found after a few

preliminary experiments that the initial concentrations of CLS should be ≥ 0.1 per cent in 30 cc of an aqueous solution for 0.5 g of the solid.

The isotherm shows a rapid increase in adsorption as equilibrium concentration increases, but it tapers off in the region between 0.05 and 0.15 per cent CLS concentration (Fig. 6). Between 0.15 and 0.30 per cent CLS there is again a steep increase in the rate of adsorption, the amount being almost proportional to the equilibrium concentration. The scanning isotherms obtained from various points show complete irreversibility up to 10 per cent adsorption. At values higher than 10 per cent desorption isotherms indicate only partial reversibility.

Figure 7 represents X-ray diffractograms of the hexagonal phase and the CLS-treated samples on the desorption branches corresponding to the net adsorption values of 10 and 24.25 per cent CLS. The hexagonal phase shows a sharp peak for C_4AH_{13} at $7.90 \text{ \AA}$ and two characteristic peaks for C_2AH_8 at $10.5 \text{ \AA}$ and $5.23 \text{ \AA}$. The presence of a peak resulting from contamination of CO_3^{2-} in C_4AH_{13} is also indicated. The 10 per cent CLS-hexagonal complex phase exhibits a sharp peak of larger magnitude at $10.5 \text{ \AA}$, but one of reduced intensity at $7.90 \text{ \AA}$. With 24.25 per cent CLS the intensity of the peak of $10.5 \text{ \AA}$ is not changed, although that at $7.90 \text{ \AA}$ is reduced with respect to the hexagonal phase.

The surface area of the hexagonal phase is $11.06 \text{ m}^2/\text{g}$. This phase, which has 10 and 24.25 per cent irreversibly adsorbed CLS, shows surface areas of 15.30 and $13.8 \text{ m}^2/\text{g}$ respectively. CLS, by itself, has a surface area of only $0.69 \text{ m}^2/\text{g}$.

Differential thermograms of the hexagonal phase, CLS-containing phase, and CLS are compared in Figure 4. The hexagonal phase shows the two typical endothermal peaks at 195 and 280°C owing to dehydration of C_2AH_8 and C_4AH_{13} . This phase contains irreversibly adsorbed CLS and exhibits, in addition to the two endothermal peaks, three exothermal peaks at about 340 , 670 and 790°C . The peak at 790°C is sharp and intense. An unmistakable endotherm with a peak at about 825°C also develops. The exothermic peaks are not present in the thermogram obtained in an atmosphere of N_2 .

Thermogravimetric analysis of some of the samples, carried out in vacuum, is shown in Figure 8. Calcium lignosulfonate loses weight rapidly in the range 200 to 400°C , and gradually between 400 and 1000°C . Of the total weight loss of 67.0 per cent, about 50 per cent of it, or 75 per cent of the total loss with respect to the starting material, occurs below 500°C . The hexagonal phase loses 34.5 per cent of its weight, whereas that containing 10 per cent CLS shows a loss of 32.5 per cent up to a temperature of 500°C . A sharp loss occurs beyond 750°C for the hexagonal phase containing CLS.

An electron microscopic examination of the hexagonal phase indicates a large number of plates (Fig. 9). This phase, treated with CLS, shows cleavage in the plates as well as some curling.

These observations of the influence of CLS on the hexagonal phase may be interpreted as follows :

Adsorption of 10 per cent CLS or less on the hexagonal phase, even at low concentrations, shows

Fig. 7. — X-ray diffractogram of hexagonal phase and that treated with calcium lignosulfonate.

Fig. 8. — TGA of hexagonal phase, hexagonal phase + CLS and calcium lignosulfonate.

complete irreversibility, indicating that the added CLS is reacting strongly as a complex with the hexagonal phase. The sample containing 10 per cent CLS that was subjected to X-ray analysis shows a decrease in intensity of the line at 7.90 Å and an increase at 10.5 Å. This must indicate that CLS enters the interlayer position of the C_4AH_{13} component and increases its c-axis spacing. When Dosch prepared C_4AH_{13} containing various organic substances he observed an increase in the c-axis spacing [31]. Young recently found that sugars also can increase the c-axis spacing in a C_4AH_{13} sample [32]. The increase in the surface area of the hexagonal phase from 11.06 to 15.30 m²/g after treatment with CLS is due to N_2 which enters the interlayer positions following an increase in the c-axis, and possibly also to some dispersion.

Comparison of the adsorption-desorption isotherm up to 10 per cent CLS adsorption shows some similarity with that of water or methanol on hydrated portland cement [33]. In the portland cement - H_2O system the irreversible component correlated well, with interlayer penetration by water and methanol into the hydrated silicates. In an N_2 atmosphere the exothermic effects of the hexagonal phase-CLS- H_2O system are annulled, showing that they represent oxidation effects. The emergence of a high-temperature exothermic effect at about 790 °C for the hexagonal phase, with irreversibly adsorbed CLS, reveals that higher temperatures are needed to oxidize the CLS complexed with the hexagonal phase. A simple calculation from the weight loss curves shows that CLS in the hexagonal phase is more resistant to decomposition than CLS alone. In the micrographs there is a definite indication that the plates have cleaved due to the stresses induced by CLS in interlayer positions.

As may be seen in Figure 6, at equilibrium concentrations beyond 0.15 per cent there is a steep increase

Fig. 9. — Electron micrographs of the hexagonal phase treated with CLS.

- a) Hexagonal phase ($\times 6300$),
- b) Hexagonal phase + 10 % CLS ($\times 6300$),
- c) Same as b ($\times 12,750$),
- d) Same as b ($\times 25,500$).

in adsorption. The possibilities envisaged include dispersion due to increased penetration of CLS into the interlayers and precipitation of CLS with a higher Ca^{++} content, as was observed in the C_3A -CLS- H_2O system at higher CLS concentrations. Several observations indicate that formation of high lime CLS is

Fig. 10. — Adsorption-desorption isotherms of calcium lignosulfonate on the cubic phase.

mainly responsible for the steep increase in CLS consumed. The pH value of the solution shows a sudden drop at adsorption values beyond 10 per cent. A brown gel was noticed in the system at adsorption values above 10 per cent. If dispersion was the main cause, the surface area values should have shown considerable increase. In fact, the surface area values were 11.06, 15.4, 15.3 and 13.8 m^2/g for the hexagonal phase containing 0, 9.0, 10.0 and 24.25 per cent CLS, respectively. As already stated, the surface area of the gel is very small. If one were to consider that the hexagonal phase with 24.25 per cent CLS partly contains the phase with 10 per cent CLS, the rest precipitating as a gel, one would expect an area of less than 15.3 m^2/g . Even with C_3AH_6 higher amounts of CLS were found to promote formation of a gel-like brownish material. Desorption of CLS at higher concentrations is due to partial solubility of the gel-like material. Although the peak effect due to C_4AH_{13} is reduced, there is no increase in the intensity of the peak at 10.5 Å in the X-ray diffractogram of the hexagonal phase containing 24.25 per cent CLS, even though this sample contains interlayer CLS. Probable explanations may be : 1) the percentage of material containing interlayer CLS is reduced because of the excess CLS (14.25 per cent) present, and 2) at excess CLS there is a possibility of dispersion effect. The intensity of the peak is not noticeable because the C_2AH_8 , with a peak at about 10.5 Å, has dispersed.

Stabilization of the hexagonal phase with respect to the cubic phase seems to depend on the amount of CLS adsorbed as a complex with the hexagonal phase in the interlayer. This CLS probably inhibits free movement of the interlayer ions responsible for conversion to the cubic form.

Tricalcium Aluminate Hexahydrate - Calcium Lignosulfonate - Water System

Preparation of the cubic C_3AH_6 is best achieved by autoclave treatment of C_3A at 100 psi for 24 hours. The hydrates obtained by boiling C_3A in H_2O continuously for 24 hours did not convert C_3A completely, presumably owing to the formation of a C_3AH_6 layer over C_3A particles. Autoclave treatment at 300 psi for 5 hours was found to form $\text{C}_4\text{A}_3\text{H}_3$ by the reaction $\text{C}_3\text{AH}_6 \rightarrow \text{C}_4\text{A}_3\text{H}_3 + \text{Ca}(\text{OH})_2$. This particular sample, when used as a starting material for CLS adsorption

studies, was found to behave in the same way as pure C_3AH_6 prepared at 100 psi in the autoclave.

Adsorption-desorption scanning isotherms are presented in Figure 10. After a rapid initial adsorption the amount is almost constant at 2.05 per cent. The scanning isotherms from different points show complete irreversibility. The surface areas of C_3AH_6 and C_3AH_6 containing 2.05 per cent CLS show values of 4.71 and 9.38 m^2/g , respectively. Electron micrographs and X-ray diffractograms did not show any perceptible difference between the two samples. The increase in surface area and the irreversibility of adsorption indicate that C_3AH_6 is dispersed in the presence of CLS. Dispersion seems to increase with concentration of CLS up to a point. The CLS seems to be chemisorbed on the C_3AH_6 surface. The total amount, however, is much less than that on the hexagonal phase. The CLS adsorbed by unit surface of the cubic phase is about 53 per cent less than that on the hexagonal phase. DTA results on the system are shown in Figure 11. The C_3AH_6 with CLS shows

Fig. 11. — DTA of the cubic phase treated with calcium lignosulfonate.

sharper endothermic peaks whether in air or in nitrogen. The ratio of the areas of the two endothermic peaks is constant for both C_3AH_6 and C_3AH_6 containing CLS. The relatively sharper peaks obtained for the C_3AH_6 containing CLS are the result of finer particle size.

At equilibrium concentration above about 0.18 per cent CLS the curve in the isotherm becomes steeper, just as it does for the hexagonal phase. This corresponds with the formation of the gel-like material already discussed.

CONCLUSIONS

In the C_3A - calcium lignosulfonate - H_2O system it is not possible to determine an adsorption isotherm. At very low concentrations CLS retards the conversion of the hexagonal to the cubic phase. At high concentrations of CLS the hydration of C_3A to the hexagonal phase seems to be inhibited by a coating of a complex of C_3A with CLS. At still higher concentrations a gel containing excess Ca^{++} and Al^{+++} is also precipitated. This gel is non-crystalline, has low surface area, and is only slightly soluble in H_2O . No evidence was obtained for the formation of a complex of composition $C_3A.CLS.H_n$ at high concentrations.

It is possible to determine an adsorption isotherm in the system, hexagonal form-CLS- H_2O , provided the concentration of CLS is kept above a particular level. Scanning loops in the isotherms show complete

irreversibility, indicating formation of an interlayer complex. The complex formation results in a higher surface area. It is more resistant to oxidation than the CLS. The interlayer complex is thought to be responsible for the inhibition of conversion of the hexagonal to the cubic form. At adsorption values beyond 10 per cent CLS a gel forms.

In the C_3AH_6 -CLS- H_2O system there is rapid adsorption of about 2.05 per cent CLS. The scanning loops show completely irreversible adsorption of CLS. Adsorption is attended by a twofold increase in the surface area of C_3AH_6 . Dispersion of C_3AH_6 and chemisorption of CLS are indicated.

The present tendency to attribute the retarding action of calcium lignosulfonate to adsorption on the C_3A phase should be altered in favour of the concept of "the consumption of calcium lignosulfonate by calcium aluminate hydrates".

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RÉSUMÉ

Effet du lignosulfonate de calcium sur l'aluminate tricalcique et ses produits d'hydratation. — L'influence du lignosulfonate de calcium (CLS) sur C_3A , C_4AH_n - C_2AH_n et C_3AH_6 a été étudiée en milieu aqueux. Il n'est pas possible d'obtenir un isotherme d'adsorption dans le système C_3A -CLS- H_2O . A de plus faibles concentrations de CLS il se forme un complexe, et aux hautes concentrations un précipité dû à la formation de CLS alcalin. Il est possible d'obtenir des isothermes d'adsorption dans les systèmes C_4AH_n - C_2AH_n -CLS- H_2O et C_3AH_6 -CLS- H_2O . Les phases cubiques et hexagonales adsorbent irréversiblement le CLS dans des proportions

respectives de 10 et 2 %, à une concentration d'équilibre de 0,15 g/100 ml. L'adsorption entre les couches et la dispersion déterminent un accroissement de surface. On a aussi observé des modifications morphologiques, ainsi que des variations de pH et des caractéristiques thermiques, dues à la migration du CLS dans les aluminates.

On propose de modifier la tendance actuelle d'attribuer l'action retardatrice du CLS à l'adsorption par la phase C_3A en faveur de « l'épuisement du CLS par les produits d'hydratation de l'aluminate tricalcique ».

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