Pergamon

Cement and Concrete Research 30 (2000) 267–273

CEMENT AND CONCRETE RESEARCH

A Fourier transform infrared spectroscopic investigation of the early hydration of Portland cement and the influence of sodium lignosulfonate

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Received 21 October 1998; accepted 18 November 1999

Abstract

The early stages of hydration of Portland cement Type I in the presence and absence of sodium lignosulfonate (a superplasticizer) have been investigated by Fourier transform infrared spectroscopic technique. Sequential experiments were performed at various times ranging from 2 min to 24 h. A number of discrete OH bands in the water stretching region and the dynamics of changes in the sulfate region during early hydration of Portland cement have been characterized. The OH stretching region on the spectra provided information on the nature of chemically bound water and the effects of sodium lignosulfonate on these entities. The results of these studies indicate that the superplasticizer prolongs the induction period and inhibits the hydration reaction. The reaction of the CSH with carbon dioxide is demonstrated by enhanced intensities of the carbonate bands. The hydration reaction seems to be controlled by dispersions of various charges present in hyperalkaline solution in cement paste. The induction period seems to be associated with an amorphous ettringite-like phase. The mechanism of inhibition is discussed in the light of a Charge-Controlled-Reaction-Model. According to this model, the Ca^{2+} ions from initial hydration go into the solution to form a bilayer of counterions with the negatively charged surfaces. Consequent to this intrinsic process, a trilayer consisting of superplasticizer anions is immediately formed, which inhibits further hydration.

Keywords: Hydration; Retardation; Portland cement; Adsorption; Hydration products

1. Introduction

The early stages of cement hydration have been of considerable interest as evidenced by a collaborative review [1] and extensive discussion in the literature [2]. Taylor has defined three periods of hydration of cement in terms of development of microstructure: (1) early period from mixing to 3 h, (2) middle period from 3 h to 24 h, and (3) the late period from 24 h to 28 days. Extensive studies of the thermal changes and concentrations of pore solutions as summarized by Taylor [2] and studies by others [3] have allowed the early and middle periods to be further divided into five stages as shown in Fig. 1. These are characterized as: a preinduction period (I) from mixing to about 20 min; the dormant stage or induction period (II) of approximate 1 to 3 h; the acceleration stage (III) up to about 12 h; the deceleration stage (IV) and the final stage (V) of slow reactions. The approximate boundaries of these stages are given in Fig. 1. In the literature there is a general agreement about the occurrence of these five stages, especially in the hydration of tricalcium silicate [3]. There is, however, considerable disagreement about the sequence of chemical changes taking place in the cement system. A significant portion of these changes in cement chemistry occurs in the first 20 min of contact with water during the preinduction period. Thomas and Double [4] and Birchall et al. [5] have reported that very early hydration (<1.0 h) involves mainly the Na^+, K^+, Ca^{2+}, OH^-, and SO_4^{2-} ions, and that gypsum dissolution accounts for much of this chemical activity. As shown in Fig 1, between $\sim$2 to 12 h the concentrations of various species change very little, indicating a balance between the continued dissolution of the cement phases and precipitation of the products. At 12 to 16 h, the concentrations of Ca^{2+} and SO_4^{2-} ions fall sharply, with a simultaneous rise in OH^- ion concentration.

There is a paucity of information on the molecular chemistry during these periods, and particularly so in the very first few minutes of hydration. The preinduction stage and the dormant stage are very important in solidification/stabilization of hazardous wastes as seen in the cases of zinc [6,7], cadmium [8], and lead [9]. These species are surface active in these stages and cause retardation of hydration by forming mixed hydroxides with Ca^{2+} ions such as $CaZn_2(OH)_6$ [6]

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0008-8846/00/$ – see front matter
PII: S0008-8846(99)00243-4

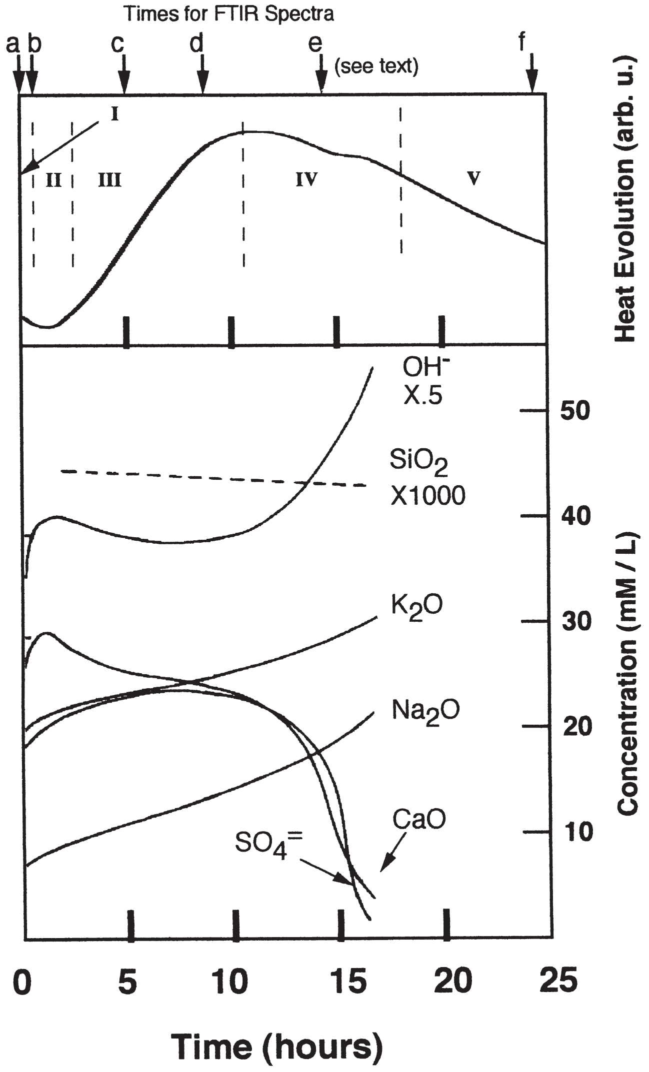

Fig. 1. Rate of heat evolution (a) and concentrations in pore solution as a function of hydration time (b). These figures are drawn based on Taylor [2] using arbitrary units. Arrows: (a) 2 min, (b) 1 h, (c) 5 h, (d) 9 h, (e) 15–16 h, (f) 24 h.

and $CaCd(OH)_4$ [8]. In continuation of our research programs to extend the use of vibrational spectroscopy for delineating the mechanisms of solidification/stabilization (s/s) of priority metal pollutants using cement-based systems, it was important to examine the hydration of cement from mixing to 24 h as indicated by the arrows labeled a through f in Fig. 1. The effects of superplasticizer (SP) on the very early hydration of cement will also be examined because of their expected strong effects on the early hydration stages.

The superplasticizers (also known as superfluidizers, super-water reducers, or high-range water reducers) are water soluble, natural or artificial polymers often used in the concrete industries as dispersing agents. The most widely used SP are: sulfonated melamine formaldehyde condensate (SMF), lignosulfonate (LS), and sulfonated naphthalene formaldehyde condensate (SNF). Modified lignosulfonates (MLS), sulfonic-acid esters, and carbohydrate esters, among others, are also used for this purpose. The mechanisms of superplasticizer (cement modifications) are being vigorously pursued [3,10,11]. There seems to be a general agreement in the literature that the dispersive action of the SP is caused by the adsorption of SP molecules on the surface of the cement grains during the initial hydration reaction [10,11]. However, the mechanisms of such adsorption are not yet clearly understood. In recent publications from the authors' laboratory we have proposed a charge-controlled reaction mechanism to explain the SP-cement interactions [12,13]. In the present article we have investigated the early hydration of Portland cement and the effect of added SP on early hydration (Fig. 1, Stages I and II) by Fourier Transform Infrared Spectroscopy (FT-IR).

FT-IR spectroscopy is one of the powerful techniques normally used for molecular characterization. Recently, FT-IR has been found to be very useful in delineating the complex chemistry involved in the hydration of cement [6,8]. In particular, the FT-IR results have been used to resolve the hydroxyl bands, in understanding the degree of silicate polymerization occurring, and in monitoring the dynamics of changes in the sulfate region during hydration reactions. Also, the effect of atmospheric carbon dioxide on hydration has been characterized.

2. Methods

2.1. Sample preparation

Portland cement (Type I) used in this investigation was supplied by Texas Industries Inc. (Dallas, TX, USA). Analytical grade sodium salt of lignosulfonic acid (LS) was received from Aldrich Chem. Co. (St. Louis, MO, USA). The chemical formula of the compound is shown in Fig. 2.

Hydrated cement samples were prepared by gradually adding deionized water to dry cement under constant stirring for a minimum time of 1 min using a hand mixer. Samples with superplasticizer (1.0% w/w) added were made first by thoroughly mixing superplasticizer with dry cement, and then by adding deionized water under constant stirring as before. A water-to-cement (w/c) ratio of 0.4 was maintained in all cases. The samples were then stored either in argon atmosphere or laboratory air. The samples were examined by FT-IR over the following time schedule: 2 min, 20 min, from 1 to 12 h (hourly), and 14 and 24 h. Three sample types were studied: cement/ambient atmosphere, cement/argon, and cement-superplasticizer/ambient atmosphere.

2.2. FT-IR analysis

Samples for FT-IR studies were mixed with predried FT-IR grade KBr (Aldrich Chem. Co., St. Louis, MO, USA) and pressed into disks. Transmission infrared spectra of the disked samples were recorded using a Genesis FT-IR instrument (ATI Mattson, Madison, WI, USA) in the region 4,000 to 400 cm^{-1} with 2.0 cm^{-1} resolution. The samples were scanned 32 times.

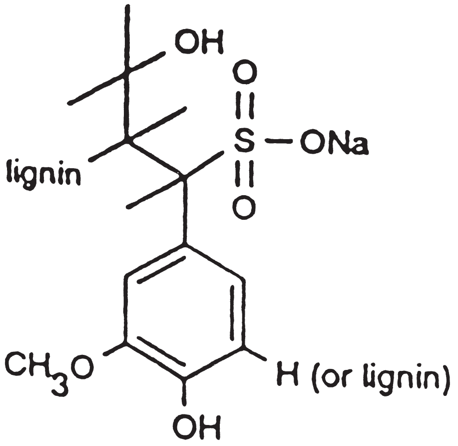

Fig. 2. Structural formula of sodium salt of lignosulfonic acid.

3. Results

The major vibrational bands identified for dry cement in the present experiments are: Si-O asymmetric stretching vibration (ν_3) of silicate, Si-O out-of-plane bending vibration (ν_4) of silicate, and Si-O in-plane bending vibration (ν_2) of silicate centered at 925, 522, and 452 cm^{-1}, respectively. The triple bands appearing in the range 1,152 to 1,096 cm^{-1} are due to S-O stretching vibration (ν_3) of SO_4^{2-}, and the weak bands at 662 and 601 cm^{-1} are due to bending (ν_2) vibrations of SO_4^{2-}. The bands at 3,645 and 1,622 cm^{-1} come from trace amount of water present. The band assignments are in good agreement with those reported in the literature [6,14,15].

The spectral data changes upon hydration and analyses of these changes can provide valuable information about the mechanisms of cement hydration. The spectral data will be discussed in three regions: the water region ($>1{,}600$ cm^{-1}), the sulfate region (ca. 1,100–1,150 cm^{-1}), and the material region ($<1{,}000$ cm^{-1}). The FT-IR spectra of hydrated cement cured in air and argon and recorded after 2.0 min are shown in Fig. 3. A representative spectrum of the superplasticizer-added sample is also shown in Fig. 3. A spectrum of pure sodium lignosulfonate (Fig. 3a) and one of dry cement (Fig. 3b) is included in Fig. 3 for clarity of discussion.

3.1. Water region ($>1{,}600$ cm^{-1})

The water region holds much of the information needed to reveal the mechanisms of early hydration of cement. It can be seen (Fig. 3) that the air-cured sample analyzed after 2 min has three bands at 3,645, 3,545, and 3,405 cm^{-1}. The bands at 3,645 and 3,545 cm^{-1} are due to metal-bonded hydroxides [8], while the one at 3,405 cm^{-1} is attributed to hydrogen-bonded OH species (O-H–O-H) adsorbed on the surfaces. The band at 3,645 cm^{-1} is due to the OH band from $Ca(OH)_2$. The argon-cured sample also shows three bands as in the case of the air-cured sample. However, the LS-added sample shows an additional band at 3,610 cm^{-1}, which possibly arises due to surface-bonded OH groups. These bands, except the one at 3,645 cm^{-1}, disappear as the hydration reaction progresses as evidenced by the FT-IR spectra (4,000–3,000 cm^{-1} range) of the hydrated samples analyzed after 2 min and 1, 5, and 24 h (shown in Fig. 4A). The broad band centered at 3,400 cm^{-1} in the 24-h-old sample is due to symmetric and asymmetric (ν_1 and ν_3) stretching vibrations of O-H adsorbed water molecules. The FT-IR spectra (4,000–3000 cm^{-1} range) of the SP-added samples analyzed after 2 min and 1, 9, and 24 h are given in Fig. 4B.

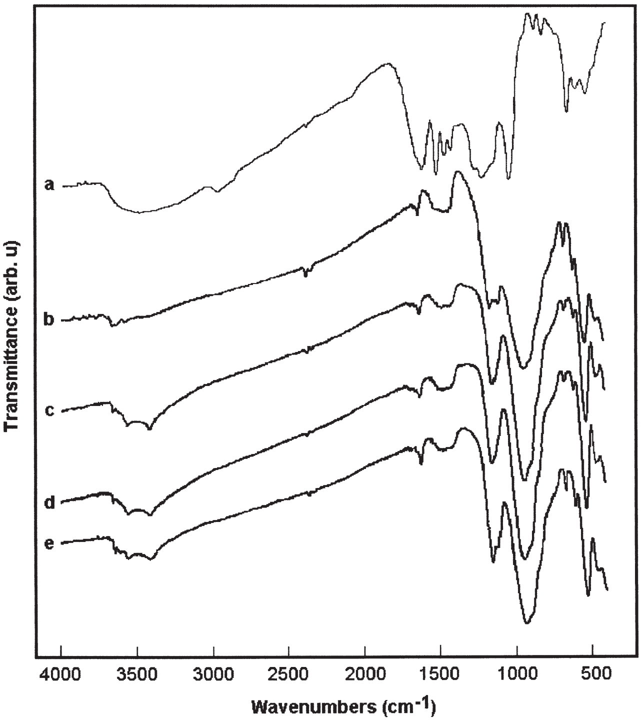

Fig. 3. FT-IR spectra of (a) pure dry sodium lignosulfonate, (b) dry cement, (c) hydrated cement prepared in air, (d) hydrated cement prepared in argon, and (e) SP-added hydrated cement prepared in air. Samples were analyzed after 2 min of preparation.

It can be clearly seen that the OH bands due to chemically bonded hydroxides disappear with the progress of hydration, but the band due to $Ca(OH)_2$ becomes stronger. The water stretching region (~3,460–3,440 cm^{-1}) becomes broader (Figs. 4A and B) with reaction time, and this is due to molecular water. From a close examination of the water region it was found that the bending vibrational band at 1,630 cm^{-1} has been shifted by about 40 cm^{-1} units in the presence of SP. The shifting of the H-O-H bending vibration in the SP-blended samples by about 40 wave number units thus indicates greater restriction due to incorporation or association of water molecules into the cement-SP matrix. This implies stronger bonding between H_2O and the host structure.

The carbonate bands, 1,420–1,480 cm^{-1} (Fig. 3) in both initial dry and hydrated samples, arise from the reactions of atmospheric CO_2 with calcium hydroxide [16].

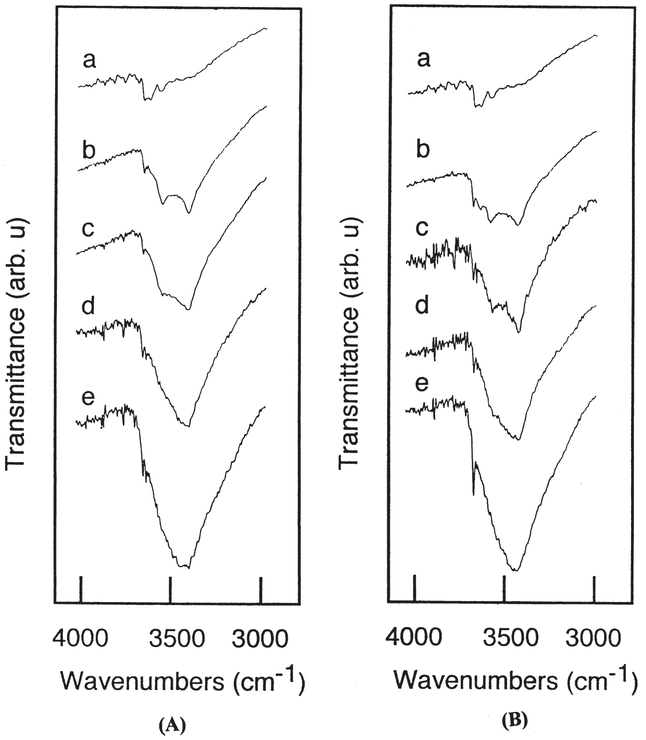

Fig. 4. FT-IR spectra of water stretching region: (A): (a) dry cement, (b) 2 min, (c) 1 h, (d) 5 h, (e) 24 h; (B): with added superplasticizer (a) dry cement, (b) 2 min, (c) 1 h, (d) 9 h, (e) 24 h.

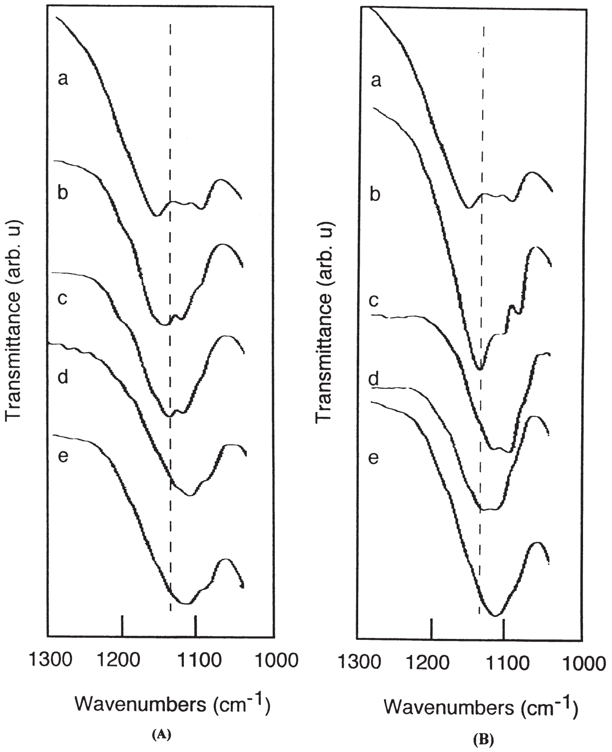

Fig. 5. FT-IR spectra of the sulfate region: (A): (a) dry cement, (b) 2 min, (c) 1 h, (d) 5 h, (e) 24 h; (B): (a) dry cement, (b) 2 min, (c) 1 h, (d) 9 h, (e) 24 h.

3.2. Sulfate region (ca. 1,100–1,150 cm^{-1})

The sulfate absorption bands (S-O stretching bands) at 1,151, 1,117, and 1,097 cm^{-1} in the dry cement change upon hydration, as can be seen in Fig. 3. The air-cured and argon-cured samples have two bands at ca. 1,145 and 1,126 cm^{-1} and a very weak shoulder at ca. 1,095 cm^{-1}. The FT-IR spectra of the sulfate region in hydrated cement samples and analyzed after 2 min and 1, 5, and 24 h are shown in Fig. 5A. The corresponding spectra of the SP-added cement samples analyzed after 2 min and 1, 9, and 24 h are given in Fig. 5B. The appearance of three bands in the 2.0-min-old sample in hydrated cement only is similar to that of the dry sample, which gradually changes into a strong band with a weak shoulder (Fig. 5).

The observance of the dynamics of changes in the sulfate (SO_4^{2-}) region is an important outcome of the present work. The changes in the sulfate region can provide valuable insight into the intrinsic mechanisms of early hydration of cement. It is known that the early formation of ettringite upon hydration is shown by a change in the sulfate absorption to a singlet, and the subsequent replacement of ettringite by monosulfate by a further return to a doublet [2]. The FT-IR spectra of the air-cured sample analyzed after 2.0 min show two strong bands at 1,124 and 1,145 cm^{-1} with a weak shoulder at about 1,100 cm^{-1}. The gradual shift of the strong sulfate band toward a lower wave number is caused by the formation of ettringite. It is interesting to note that the sample made with LS shows three bands when analyzed after 2.0 min that turn into two bands after about 1 h and finally into one band after about 24.0 h. This observation clearly indicates very little reaction occurring in the presence of LS during the first 2.0-min period of hydration. This will be further supported by the fact that the silicate region did not undergo any significant changes in the LS-added samples (Fig. 3).

3.3. Materials region (<1,000 cm^{-1})

The bands at 925, 525, and 455 cm^{-1} in dry cement also undergo changes upon hydration. The shifting of the Si-O asymmetric stretching (ν_3) vibration to higher wave numbers and the changes in the relative intensities of the Si-O out-of-plane bending vibration (ν_4) and in-plane bending vibrations (ν_2) indicate polymerization of the silicate units (SiO_4^{4-}). This shifting of the Si-O stretching vibration (ν_3) to a higher wave number is considered as fingerprint evidence for the degree of polymerization with the formation of C-S-H phase as a result of hydration of cement. This shifting of the Si-O stretching band, due to polymerization in hydrated cement, eventually obscures the SO_4^{2-} bands in the 1,138 to 1,155 cm^{-1} region. However, close examinations of the FT-IR bands in the air-cured, argon-cured, and LS-blended cement reveal that the Si-O stretching band in these samples appears at around 930 ± 2 cm^{-1} in 2.0-min-old samples, which are very close to the similar band in the dry cement. Also, the relative intensities of the Si-O out-of-plane bending vibration (ν_4) and in-plane bending vibration (ν_2) did not undergo any significant changes. Thus it indicates very little polymerization of SiO_4^{4-} in 2.0-min-old samples. The Si-O stretching band shifts as the hydration progresses, and in 24.0-h-old samples this band has been shifted by ca. 10 cm^{-1} units only, indicating that there has been very little polymerization of the silicates in these samples. This is further supported by the appearances of strong SO_4^{2-} bands centered at 1,114 cm^{-1}.

4. Discussion

The observance of a number of discrete OH bands during early hydration of Portland cement and the dynamics of changes in the sulfate region are the two most important outcomes of the present research. The OH band appearing at 3,645 cm^{-1} has been positively identified to be due to $Ca(OH)_2$. In analogy to the adsorption of water or hydroxyl groups on passive layers formed on iron [17], we believe that these OH bands are due to chemically bound water on the membrane or at the surface of the gel-like membrane proposed by Thomas and Double [4] and Birchall et al. [5]. The disappearance of these OH bands with increasing hydration time at the end of the induction period clearly suggests that the layers of chemically bound water may control the movement of different ionic species and water present in the system across the layer, as well as the progress of cement hydration.

It is pertinent to mention at this stage that the "osmotic membrane model" was proposed by Thomas and Double [4] based on pore solution analyses and measurements of thermal changes by conduction calorimetry during cement hydration. It is visualized that a "colloidal gel membrane" is formed by precipitation at high local levels of supersaturation between calcium ions in solution and the hydrolyzed silicate-rich surfaces of the silicate grains. They assumed that this reaction provides a protective C-S-H gel around the cement grains that initially retards the reaction. This initial stage of retardation is known as the "dormant/induction" period. The gel membrane is regarded as permeable to water only, and subsequent growth of silicate hydrates takes place as a result of inward flow of water by occasional rupture/burst of the membrane caused by osmotic pressure differential on either sides of the membrane. These conclusions were also supported by Birchall et al. [5].

The suppression of "flash set" of cement by the addition of gypsum was also explained by this "gel membrane osmotic model" [5]. It is believed to be due to the formation of "a very insoluble type of ettringite" on C_3A surfaces. The formation of a gelatinous surface layer is a largely accepted concept in explaining the early hydration of cement, although no definitive evidence is yet known about the exact composition of these gelatinous materials. However, it can be predicted that the gelatinous materials must be composed of Ca^{2+}, AlO_4^{2-}, SO_4^{2-}, and OH^-, with other possible cations such as K^+ and Na^+, where some Ca^{2+} and most of the SO_4^{2-} are introduced from the gypsum added to the cement system. The FT-IR characterization of the early hydration in the present case provides definitive evidence that the gelatinous surface film is, at least, partly composed of metal hydroxides and chemically bound water. The broadness of some of the peaks and their location at lower energies at 3,610, 3,555, and 3,410 cm^{-1} suggests that hydrogen bonding may also be involved. The latter considerations point toward an amorphous ettringite-like layer as the cause of the induction period and one that does not necessarily involve silicate anions.

The hydration of cement is characterized by a number of stages, especially at the very early period of reaction as already outlined in the introduction section. The FT-IR data indicates that the "dormant" or induction period extends up to ~4 to 5 h as reflected by the changes in the sulfate region (Fig. 5). This induction period has been prolonged in the presence of superplasticizer, which is direct evidence that the hydration is inhibited under these conditions. The mechanism of inhibition is discussed in the following section.

The four main phases in Portland cement are: tricalcium silicate (C_3S, alite), dicalcium silicate (C_2S, β-belite), tricalcium aluminate (C_3A), and calcium aluminoferrite (C_4AF). They are usually present in the 50 to 70%, 20 to 30%, 5 to 12%, and 5 to 12% range (weight%) [18]. Small quantities, ca. 5%, of other oxides are also present. Tricalcium aluminate is an important phase in cement, which undergoes rapid hydration immediately after contact with water. The C_4AF phase is known to react with gypsum at a much slower rate than C_3A to produce ettringite. Hydration of C_3A in presence of gypsum initially produces the sulfate-containing phase ettringite ($C_6AS_3H_{32}$, AFt phase). The ettringite phase is unstable under these conditions and gradually converts into the more stable monosulfate (C_4ASH_{12}, AFm phase). The essential reactions are:

$$3CaO \cdot Al_2O_3 + 3CaSO_4 \cdot 2H_2O + 26H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O \text{ (Ettringite, AFt phase)}$$

$$3CaO \cdot Al_2O_3 + 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O \rightarrow 2(3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O) + Ca^{2+} + SO_4^{2-} + 8H_2O \text{ (monosulfate, AFm phase)}$$

The unreacted C_3A reacts with the liberated Ca^{2+} and SO_4^{2-} ions to form additional monosulfate:

$$3CaO \cdot Al_2O_3 + Ca^{2+} + SO_4^{2-} + 12H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O \text{ (monosulfate)}$$

The reactions of C_3S and β-C_2S begin in earnest after about ca. 4.0 h to form C-S-H and $Ca(OH)_2$ (CH), which cause further strengthening of cement [2]. However, the course of early hydration of aluminate phase is expected to affect considerably the eventual physical and chemical properties of the hardened Portland cement. The FT-IR results presented above show that the water and the sulfate regions in LS-added samples remain practically unchanged in

2.0-min-old samples. Also, the silicate region did not undergo any significant change. However, with time the structures of the water, sulfate, and silicate regions were significantly changed as exemplified by the FT-IR spectra recorded at various times. These observations clearly indicate that the initial hydration is inhibited by added LS, and this will be discussed in the following section.

Cement particles upon contact with water undergo very rapid reactions and immediately form thin films of unknown composition and structure on the surface of the hydrating cement particles. Eventually calcium-silicate-hydrate (CSH) phase will be formed and this will possess a negative charge because the zero-point-charge (zpc) of the silicate minerals in the cement system is much below the pH (13 ± 0.5) of cement paste. Abundant quantities of Ca^{2+} ions are present in cement-pore solution, which are extruded from inside the solid through the C-S-H membrane. These oppositely charged Ca^{2+} ions immediately form layers of positive charges against the negatively charged calcium silicate hydrate as well as calcium aluminate surfaces to constitute "Electrical Double Layers" [12]. Due to electrostatic reasons the negatively charged LS anions will concentrate against the bilayers formed by the Ca^{2+} ions.

Since the negative surface is charge compensated by Ca^{2+} ions that form an electrical bilayer, the Ca^{2+} ions released from the system will not be available for reactions to form $Ca(OH)_2$, which in effect will reduce pH of the medium. Removal of Ca^{2+} ions from solution will also prevent them from entering into setting and curing reactions in hydrating cement systems, thus inhibiting or retarding the hydration.

The concept of the "Charge-Controlled-Reaction Model" has been discussed in previous publications [12,13,19]. This reaction model has been used to successfully explain the surface precipitation of calcium zincate $\{CaZn_2(OH)_6 \cdot H_2O\}$ and calcium cadmiate $\{CaCd(OH)_4\}$ in Zn- and Cd-doped cements, respectively [6,8]. We wish to further address this reaction model in future publications, which are now in progress.

5. Conclusions

The conclusions drawn from the current research may be summarized as follows:

1. The initial contact of cement particles with water produces a surface-modified zone that has several types of bound hydroxyl groups.
2. These hydroxyl groups are maintained well into the dormant period.
3. The formation of ettringite is evidenced by the changes in the sulfate bands. The FT-IR data indicates that it is well established by about 5 h in plain cement and by about 9 h in SP-treated cement.
4. The presence of SP in the hydrating cement system stabilizes and extends both the preinduction stage and the dormant stage to longer times, as well as stabilizes the $Ca(OH)_2$ well into the IV period.

In general terms the gel-like membrane proposed by Thomas and Double [4] and much discussed by Birchall et al. [5] appears to have considerable specifically bound water reminiscent of the gel found in passive film structures [17]. Further work is necessary to assign the OH bands and delineate the structural nature of the induction stage gel-like membrane.

Acknowledgments

The authors acknowledge financial support from the Gulf Coast Hazardous Substances Research Center, Project 104LUB0437, Lamar University, Beaumont, TX, and The Robert A. Welch Foundation (Houston, TX). This material is also based in part upon work supported by the Texas Advanced Research (Technology) Program under Grant No. 003658-344.

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