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Hydrating OPC/CSF Blends: An Infrared Spectrophotometric Study

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ABSTRACT:

This paper describes the background to, and the results of an investigation of the hydration process in ordinary portland cement/condensed silica fume (OPC/CSF) blends, using the relative concentration of calcium hydroxide as a parameter and Fourier Transform Infrared Spectrophotometry (FTIR) as the investigative tool.

The study shows that the participation of silica fume in the hydration process commences within the first hour after the addition of water to the blend and provides some insight into the role of CSF concentration on the hydration process in OPC/CSF blends.

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HYDRATING OPC/CSF BLENDS:
AN INFRARED SPECTROPHOTOMETRIC STUDY

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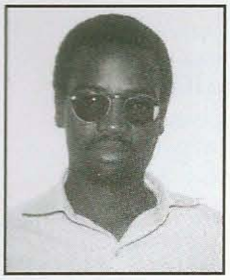

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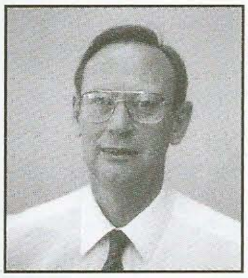

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SYNOPSIS

This paper describes the background to and the results of an investigation of the hydration process in ordinary portland cement/condensed silica fume (OPC/CSF) blends, using the relative concentration of calcium hydroxide as a parameter and Fourier Transform Infrared Spectrophotometry (FTIR) as the investigative tool. The study shows that the participation of silica fume in the hydration process commences within the first hour after the addition of water to the blend and provides some insight into the role of CSF concentration on the hydration process in OPC/CSF blends.

INTRODUCTION

The principles of FTIR and its potential as an investigative tool in the study of materials based on portland cement, were described in a paper in this journal (Morris and Kumming, 1994). In order to follow the changes in the relative concentration of calcium hydroxide during the first 28 days of the hydration process it was necessary to adopt a technique for stopping the hydration process at appropriate times, drying the sample and then recording the spectrum of the partly hydrated blend.

The technique of freeze-drying is commonly used in other fields of research, for example, organic chemistry, but appears not to have been used extensively in cement research (Rashed and Williams, 1991). Its application in cement research was described by Morris and Bergesen (1994). Essentially it relies on the fact that cooling reduces the rate of most chemical reactions and that sublimation, under vacuum, of the water from the frozen reaction mixture, dries the paste without allowing the reaction to recommence. The authors believe it holds an advantage over other techniques such as oven-drying which might accelerate the reaction before the concentration of water has dropped sufficiently to stop further development. Similarly the use of alcohol (generally isopropanol) to remove water might contaminate the sample sufficiently to complicate the infrared spectrum. The freeze-dried samples were, subsequently, briefly dried by infrared radiation to ensure that the last vestiges of water had been removed.

The pastes that were prepared for this investigation were sealed in polyethylene bags to prevent loss of water during the hydration process. They were, at appropriate stages of hydration, dipped into liquid nitrogen, instantly freezing them and reducing the temperature to around -190°C. The frozen samples were then subjected to vacuum drying while being maintained at a temperature of -40°C.

The dried, partially hydrated material could then be prepared for examination by FTIR in the knowledge that, in the absence of water, the reaction would not recommence.

The samples were mixed with potassium bromide which is transparent to infrared radiation between 5000 and 250 cm^{-1} wavenumbers (2 to 40μm wavelength). Pellets of these mixtures were then formed in a die under pressure and examined by recording their infrared absorption spectra; (Morris and Kuming, 1994).

The relative concentrations of calcium hydroxide were determined by reference to the intensity of the absorption peak caused by calcium hydroxide at 3642cm^{-1}. The relationship between calcium hydroxide concentration and duration of hydration was determined and is illustrated later in this paper.

SILICA FUME:

Silica fume or Condensed Silica Fume (CSF) condenses from the vapours from the arc furnaces during the production of elemental silicon and of ferrosilicon. It is a largely amorphous powder, finer than tobacco smoke, consisting of silicon dioxide (>85% SiO_2). Due to its extreme fineness (about 20 000 m^2/kg) (Malhotra and Carette, 1982) it is difficult to handle and it is 'densified' by agglomeration thereby increasing its density by a factor of three (from 0,2 tons per m3 to 0,6 tons per m3) it may also be made more manageable by adding water to form a slurry.

The addition of silica fume to concrete was first reported in Norway in the late 1940s (Aitcin, 1983). By 1978 the Norwegian Standards were amended to allow the use of up to 8% silica fume in an OPC/CSF blend in concrete.

In South Africa it is marketed as 'CSF 90' and contains more than 90% SiO_2.

The reasons for its use as an extender in concrete stem from the origins of hydraulic cements, namely the use, by the Romans, of mortars based on lime and natural 'Pozzolans' which were the ash spewed out by Mount Vesuvius and found in the neighbourhood of Puteoli (Pozzuoli) - hence pozzolans (Domone, 1994). The acidic silica reacts with the basic slaked or hydrated lime (calcium hydroxide, $Ca(OH)_2$) to form calcium silicate hydrates. These in turn act as hydraulic binders.

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It is, however, relatively expensive and that precludes its general use as an extender and limits its applications to the achievement of special properties.

HYDRATION OF OPC:

The phase composition of the clinker from which commercial OPC is made, is generally accepted as being represented by the Bogue formulation which in the case of South African cements may be as shown in Table 1.

When water is added to OPC various complex chemical reactions take place. However, the main products that are of interest in this study are the formation of calcium silicate hydrates which constitute the main cementitious binders, and the formation of calcium hydroxide as a product of the hydration of OPC which causes the high pH (>12), of hydrated cement.

This availability of calcium hydroxide leads to the pozzolanic reaction with CSF to produce additional calcium silicate hydrates.

It may be anticipated that the free calcium oxide in the OPC would form calcium hydroxide almost instantaneously upon the addition of water. Because the concentration of free calcium oxide in OPC is low, this contribution to the concentration of calcium hydroxide in the hydrating OPC paste would be small.

The hydration of the other components of the OPC would lead to a steady increase in the concentration of calcium hydroxide until it, asymptotically, approached a maximum value. At a later stage one might anticipate a slow reduction in the concentration as carbonation of the calcium hydroxide due to reaction with atmospheric carbon dioxide progressed. This was however, unlikely to affect the results of our investigation since the pastes would not be exposed to the atmosphere and the experiment would only examine the first 28 days of the hydration process.

HYDRATION OF OPC/CSF BLENDS:

It was anticipated that the rate of production of calcium hydroxide resulting from the hydration of the OPC in the OPC/CSF blend would be very similar to that arising from the hydration of unblended OPC but that when the concentration of calcium hydroxide reached an appropriate level the pozzolanic reaction with the CSF would commence.

Since the reaction between silica fume and calcium hydroxide to form calcium silicate hydrates could be expected to reduce the concentration of calcium hydroxide in the hydrating OPC/CSF blend, a comparison of the concentrations of calcium hydroxide in hydrating OPC and in hydrating OPC/CSF blends should show at what stage the pozzolanic reaction involving CSF commences.

EXPERIMENTAL PROCEDURE:

For this investigation a series of OPC/CSF blends were prepared on the basis of addition of CSF to OPC:

TABLE 1: COMPOSITION OF SOUTH AFRICAN OPC BY MASS.

Abbreviation	Compound	Formula	% by mass in cement
C_3S	Tricalcium silicate	$3CaO.SiO_2$	35 - 55
C_2S	Dicalcium silicate	$2CaO.SiO_2$	20 - 40
C_3A	Tricalcium aluminate	$3CaO.Al_2O_3$	5 - 12
C_4AF	Tetracalcium aluminoferrite	$4CaO.Al_2O_3.Fe_2O_3$	5 - 10
C	Calcium oxide or Free lime	CaO	0,5 - 2,5
M	Magnesium oxide or magnesia	MgO	0,3 - 4
$C\bar{S}H$	Calcium sulphate or Gypsum	Raw material	4 - 7

(Addis, 1994, adapted)

TABLE 2 COMPOSITION OF EXPERIMENTAL OPC/CSF BLENDS BY MASS

Blend NO	W/(OPC+CSF)	OPC	CSF	OPC+CSF	% CSF	Water
C-0	0,4	100	0,0	100,0	0	40
E-1	0,4	100	2,5	102,5	2,4	41
E-2	0,4	100	5,0	105,0	4,8	42
E-3	0,4	100	10,0	110,0	9,1	44
E-4	0,4	100	15,0	115,0	13,0	46
E-5	0,4	100	20,0	120,0	16,7	48

For this study the ratio of water to cementitious material was kept constant at 0,4 by mass. Distilled water was used and no super-plasticiser or other additive was used.

Each dry blend was mixed thoroughly in a kitchen blender (Kenwood Chef) at low speed for three (3) minutes. Experiment showed that this consistently produced a blend of even colour.

The requisite amount of water was added and the paste was mixed at high speed for 5 to 8 minutes. The mixing time was increased for the higher concentrations of CSF to attain consistent mixing as the increased CSF content reduced the workability, (the mixture became increasingly sticky).

The paste was removed from the mixing bowl and sealed as a thin layer in a flat polyethylene bag, providing a large surface area for effective heat transfer in the constant temperature water bath during curing. The water bath was maintained at 25° ± 2°C.

The paste samples were allowed to hydrate for periods of 1,3,6, and 10 hours and 1,3,7,14, and 28 days before freeze drying commenced. At the prescribed times the samples were transferred to glass tubes and immersed in liquid nitrogen. When the samples were frozen, the tubes were connected to the vacuum system of the freeze drying apparatus where the water was sublimed off at a temperature of about -40°C overnight. To ensure that the samples were completely dry they were heated in an infrared oven (still under vacuum) for 5 minutes.

Such stringent procedures for drying the samples are needed to avoid further hydration and also because

Calcium Hydroxide

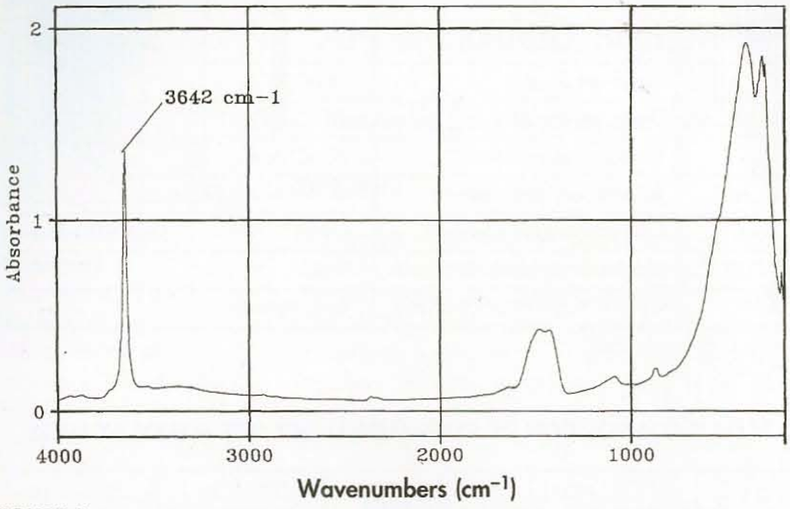

FIGURE 1

Condensed Silica fume

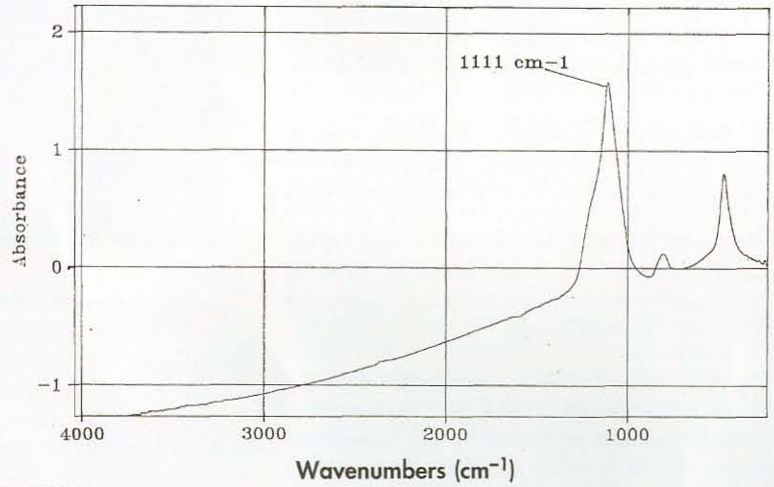

FIGURE 2

Unhydrated OPC

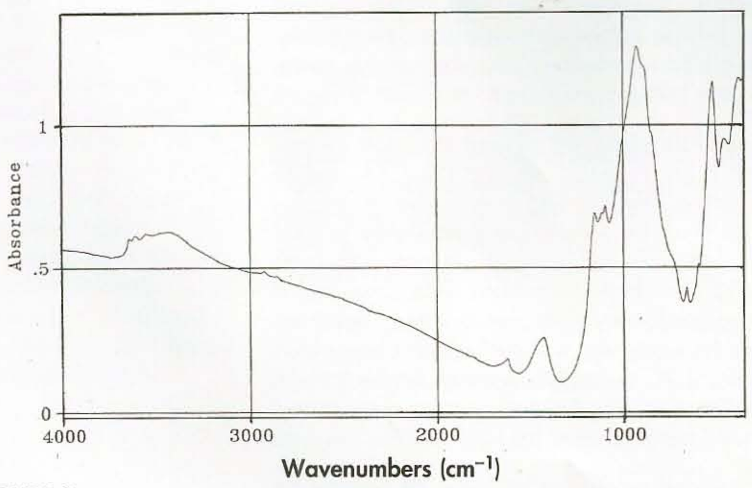

FIGURE 3

moisture absorbs infrared radiation strongly in a broad band that would tend to mask the absorption peak of calcium hydroxide at 3642 cm^{-1}. Once they had been dried the samples could be kept in a desiccator over silica gel until it was convenient to record the spectra.

The dried samples were accurately measured out on a semi-micro balance and mixed with potassium bromide (infrared grade) which had been dried in an oven at 120°C overnight, in the ratio of 2% sample and 98% KBr, using a vibratory mill (Specamill) that both mixed and ground the powders together.

The powdered sample/KBr mixture (200 mg in total) was transferred to a die in which it was subjected to high pressure under vacuum (650 MPa) for 2 to 3 minutes. This produced an almost clear pellet, 13 mm in diameter and 0,5 mm thick. The pellets could be stored in a desiccator or oven, until required.

RECORDING OF SPECTRA:

The spectrum of a pure KBr pellet was used to establish the background spectrum of the atmosphere in the spectrometer (a reference spectrum which is automatically subtracted from subsequent spectra by the software controlling the spectrometer). Then the spectra of the pellets were recorded under the same instrumental conditions namely between 5000 cm^{-1} and 400 cm^{-1}, at a resolution of 8 cm^{-1} and using 25 co-added repetitive scans. This was repeated four times for each sample and the average spectrum computed for each sample.

Spectra of pure calcium hydroxide (Fig 1), pure CSF (Fig 2), and unhydrated OPC (fig 3) were also recorded. The sharp absorption peak at 3642 cm^{-1}, due to the presence of calcium hydroxide, is clear in Fig 1, while the strong peaks due to CSF at 1111 cm^{-1} and at 800 cm^{-1} are prominent in Fig 2. The more complex and unresolved absorption peaks due to C_2S, C_3S, C_3A and C_4AF dominate the spectrum of unhydrated OPC, from about 1500 cm^{-1} to 600 cm^{-1}, in Fig 3. The presence, in the spectrum of unhydrated OPC, of minor peaks in the regions of 1111 cm^{-1} and 800 cm^{-1} would complicate the quantitative estimation of the amount of unreacted CSF in the various stages of hydration of the blend.

Fig 4 shows the progress of hydration in the 5% CSF blend.

The height of the calcium hydroxide peak at 3642 cm^{-1} relative to the baseline of the spectrum at 3700 cm^{-1}, was measured and used as an indication of the relative concentration of the calcium hydroxide.

The measured intensities of the peaks were normalised to refer to a constant OPC amount in the pellets to compensate for the fact that increasing the CSF concentration in the pastes reduced the OPC content of the pellets and affected the overall intensity of the spectra.

In Figures 5 and 6 the development of calcium hydroxide based on the intensity of the absorbance at 3642 cm^{-1} as derived from the recorded spectra, is set out in the form of a graph of time in hours (0-24 hours) and days (0-28 days) versus absorbance. Absorbance is related to concentration according to the following equation: **A = abc** (Federation of Societies for Coatings Technology, 1980); where:

A = Absorbance.
a = absorptivity and is specific to the particular material at the specific wavenumber.
b = pathlength through the sample.
c = concentration of the material that absorbs at the specific wavenumber.

Since the amount of cement in each pellet is kept constant and the thickness of the pellets are constant, the absorbance is directly proportional to the concentration of the material sought; in this case calcium hydroxide.

The concentration of calcium hydroxide generated in the OPC paste shows the expected gradual increase, the rate of which slows down after 7 days (Fig 5).

The blends show slightly lower calcium hydroxide concentrations than the OPC. After 3 hours and after 6 hours the 2,4% and 4,8% CSF blends continue to reflect slightly lower concentrations than the OPC. However, the 13,6% and 16,7% CSF blends reflect a reduction in the relative concentrations of calcium hydroxide. Since the concentrations have been normalised these lower values suggest that some of the calcium hydroxide has reacted and disappeared as a molecular species.

The higher value found for the 13,6% CSF sample after 10 hours appears to be a rogue value and would need to be re-examined. The preparation of the pellet was repeated with fresh material from the dried sample but the absorbance measured was the same.

If it were closer to that of the 16,7% CSF sample after 10 hours, the development of calcium hydroxide would appear more consistent and link up with the fact that the concentrations for all the blends reach similar values after 24 hours.

From 24 hours to 3 days there is a sharp increase in the concentration of calcium hydroxide in all the blends but with a clear indication that the higher the concentration of CSF the more rapid the development of calcium hydroxide.

From 3 days to 7 days there is a marked decrease in the calcium hydroxide concentration in all the blends except that with the lowest (2,4%) CSF content. This sample rejoins the calcium hydroxide content level and rate of production of the OPC sample.

After 7 days the three blends (4,8%, 13,6%, and 16,7%) seem to stabilise at a rate of production similar to that of the OPC sample but at a lower concentration of calcium hydroxide. Whether this trend continues will have to be investigated by an extension of the work to beyond the 28 day limit that was adhered to in this study.

4,8% CSF: 1 - 28 Days Hydration

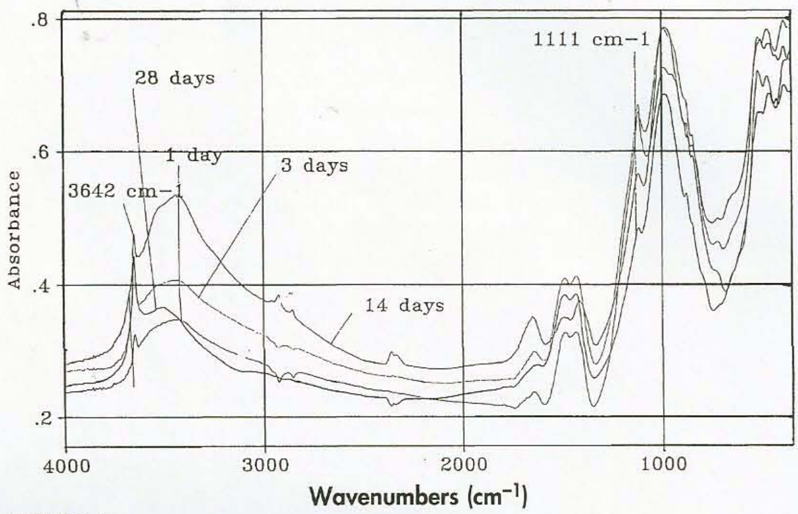

FIGURE 4

DEVELOPMENT OF CALCIUM HYDROXIDE

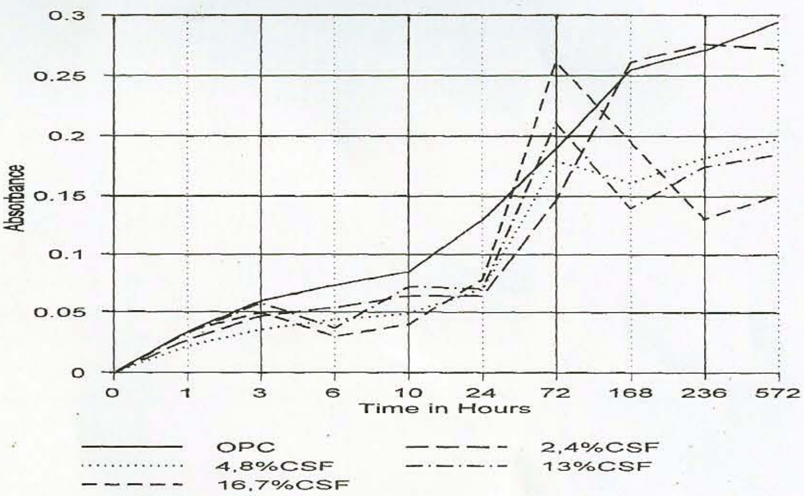

FIGURE 5

DISCUSSION:

It would seem that the lower initial concentration of calcium hydroxide in all four blends is due to the removal of Ca(OH)$_2$ as a molecular species from the reacting paste by its reaction with the pozzolanic CSF to form calcium silicate hydrates.

The reduction in the concentration of Ca(OH)$_2$ between the 3rd and 10th hours in the blends with 13,6% and 16,7% CSF might be ascribed to the reactivity of the CSF. Its greater concentration in these two blends causes it to react faster with the calcium hydroxide than the latter can be produced by the hydration of the OPC. This might also be dependent on the availability of a particularly fine and hence highly reactive fraction in the CSF.

Ramachandran (1987) reported that his calorimetric studies revealed a peak in the rate of heat generation, and therefore, of chemical reactivity, after two hours and ascribed this to the reaction between $Ca(OH)_2$ and CSF. Wu and Young (1984) suggest that the pozzolanic action of CSF arising from the hydration of C_3S, starts after two hours. Sarkar and Aitcin are reported (Rashed and Williamson, 1991) to describe CSF as a fast-reacting pozzolan. Roy (Rashed and Williamson, 1991) claims that due to its high surface area, silica fume partially dissolves in saturated calcium hydroxide solutions within 5 minutes after mixing and that a silicon-rich hydrated form is deposited as layers or films on the silica particles.

Other authors (Zhang and Gjorv, 1991) (Yogendran et al, 1991), quoting studies based on a variety of techniques, disagree and maintain that the pozzolanic reaction involving CSF only commences 1 day after water has been added to the blend. The ACI (American Concrete Institute Committee 226, 1987) maintains that the main contribution by CSF is only perceptible between 3 and 28 days after hydration starts.

Sellovold *et al* (1991) found that the CSF participation becomes significant after several days and that the maximum concentration of calcium hydroxide is reached after 7 days, whereafter it declines.

These differing results may be due to the different techniques and/or the different materials used. However, from the literature it is evident that the very early stages of the hydration reaction have not been studied as extensively as the later stages. We believe that our adoption of the technique of freez-drying the pastes in combination with FTIR analytical techniques has made these early stages accessible to our investigations.

Reference to the silica absorption peak at 1111cm^{-1} in the recorded spectra for all the blends shows clearly that the concentration of silica decreases progressively from the first hour and by the 28th day the initially strong and distinct peak has become a shoulder on the silicate peak at 1000 cm^{-1} as exemplified by the spectral series for 4,8% CSF (Fig 4) despite the noted presence of a small peak at 1111 cm^{-1} in unhydrated OPC. This bears out our contention that the CSF participates in a pozzolanic reaction within the first hour of the commencement of hydration.

A mechanism that has not been mentioned yet is that due to the so-called 'fine-filler effect'. It has been argued that the presence of fine material such as CSF can increase the rate of cement (OPC) hydration by providing nuclei on which calcium hydroxide can precipitate thereby reducing the concentration of $Ca(OH)_2$ in solution and shifting the equilibrium of the hydration process to produce more calcium hydroxide (Massazza, 1980). This might explain the rapid development of calcium hydroxide in the period between 1 day and 3 days and the apparent correlation between the concentration of calcium hydroxide and the amount of CSF in the blend. Stein and Stevels (Takemoto and Uchikawa, 1980) report that the presence of amorphous silica accelerates the hydration of C_3S and explain this by suggesting that the presence of the amorphous silica reduces the calcium and hydroxyl ion concentrations in the liquid phase, leading to the formation of products of low Ca/Si ratio and the stimulation of the hydration of C_3S. This argument is supported by Kurdowski and Nocum-Wczelik (Ramachandran, 1987) who refer to the existence of a quasi-stationary supersaturated layer of calcium ions around the C_3S.

Removal of calcium ions from this layer would stimulate the hydration of the C_3S to restore the supersaturated state. Other authors extend this line of argument to include the hydration of C_3A and C_4AF (Hjorth, 1982) (Grutzeck et al, 1983) (Cheng-Yi and Feldman, 1985).

CONCLUSION:

It seems clear from the investigation described and the work of the many other authors on the subject, that the presence of CSF in OPC paste affects the hydration process in several ways.

1 The availability of fine silica particles provides nuclei on which calcium hydroxide is precipitated from solution thereby changing the equilibrium conditions and stimulating the more rapid production of calcium hydroxide through the accelerated hydration of the OPC constituents.

2 The chemical reaction between silica and calcium hydroxide in solution, which is known as the pozzolanic reaction, commences within the first hour of the additon of water to the OPC/CSF blend.

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