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AND STOICHIOMETRY
OF BOTTLE-HYDRATED Ca_3SiO_5**

by

R. F. Feldman and V. S. Ramachandran

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A STUDY OF THE STATE OF WATER AND
STOICHIOMETRY OF BOTTLE-HYDRATED Ca_3SiO_5

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ABSTRACT

The state of water in hydrated C_3S is studied by Differential Thermal Analysis and Thermo Gravimetric Analysis techniques. Samples were conditioned at several relative humidities for lengthy periods starting from d-dry, 100 per cent R.H. and 11 per cent R.H. It was found that the stoichiometry of the bottle-hydrated C-S-H gel at 11 per cent R.H. approached from 100 per cent R.H. is $3.28 \text{ CaO} : 2\text{SiO}_2 : 3.92\text{H}_2\text{O}$. Results suggested that at higher humidities higher hydrates exist which decomposed on drying at relative humidities below 40 per cent R.H. Decomposition might occur at humidities above this level.

On étudie l'état de l'eau dans le C_3S hydraté à l'aide de l'analyse thermique différentielle et de l'analyse thermogravimétrique. Des échantillons sont conditionnés à divers degrés d'humidité relative (h.r.) pendant de longues périodes à partir de l'état "d-dry", d'une h.r. de 100 pour cent et d'une h.r. de 11 pour cent. La stoechiométrie du gel C-S-H hydraté en bouteille, à une h.r. de 11 pour cent atteinte à partir d'une h.r. de 100 pour cent, est $3,28 \text{ CaO} : 2\text{SiO}_2 : 3,92 \text{ H}_2\text{O}$. Les résultats suggèrent qu'il existe, à des degrés d'humidité plus élevés, des hydrates supérieurs qui se décomposent en séchant à une h.r. de moins de 40 pour cent. La décomposition pourrait se produire à une humidité de plus de 40 pour cent.

Introduction

A study of the stoichiometry of hydrated C_3S and the reaction of C_3S with water has always been difficult because of the problem of separating and estimating quantitatively the various products and the reactants. The equation for the reaction is of the following form:

It has been difficult to determine the amount of CaO associated with each of the two products and thus the amount of water associated with $Ca(OH)_2$. A more problematical question is to distinguish quantitatively the unreacted water from the constitutional water in the calcium silicate hydrate product, viz. $(x + Y - 3)$ molecules.

No real attempt has been made previously to estimate the total hydrate water in the C-S-H phase. (1) Previously, the stoichiometry of the C-S-H phase was determined at the d-dried condition. It was assumed that little or no free or adsorbed water remained on the sample at this condition which was the vapour pressure of water at the sublimation temperature of solid CO_2 ($-78^\circ C$) (2). In addition it would be useful to determine the stoichiometry at higher relative humidity conditions, because the stability of higher hydrates if they exist may govern and explain the behaviour of hydrated portland cement under various practical conditions of load and environment.

In a recent paper (3) it was shown by thermal analysis that higher hydrates do exist at humidities above the d-dry state for hydrated portland cement; in this present paper the stoichiometry and stability of the hydrates of C_3S at various conditions of exposure are examined by that technique. The possibility of sulphoaluminates being the cause of various phenomena is eliminated with C_3S . Relative humidity of 11 per cent on drying from 100 per cent R.H. was used as the main reference for the hydrate for experimental convenience and because, at this point, the estimate of adsorbed water can be made with some confidence.

ExperimentalMaterials

The hydrated C_3S preparation used in this work was obtained by bottle-hydrating C_3S at $23^\circ C$ for 17 months at a water-to-solid ratio of 5. The bottle-hydrated slurry was filtered and dried over 11 per cent R. H. ($LiCl$ saturated solution) and screened over a 100-mesh sieve. The residue of large $Ca(OH)_2$ crystals was ground and remixed with the powder. It was completely hydrated; carbon dioxide content was 1.4 per cent based on the weight at 11 per cent R. H. on first drying. The surface area by nitrogen adsorption was $70.3 m^2/gm$ for the d-dried sample. The sample was conditioned at 11 per cent R. H. followed by vacuum drying and finally by heating at $110^\circ C$ for 3 hr prior to surface area determination.

Sample Conditioning

Basically 4 series of samples were prepared and designated A, B, B(R) and C. The following diagram illustrates designation of samples and their history. The bottle-hydrated powder was conditioned at 11 per cent R. H. in a desiccator for 10 months and designated Preparation A.

One portion of Preparation A was spread 2 to 3 mm thick in dishes and d-dried in a large desiccator for 5 weeks. The material was then placed in a vacuum vessel and heated for 3 hr at $100^\circ C$. This sample was

designated Preparation B. Another portion of Preparation A was placed in a desiccator for two months at 100 per cent R.H. and was designated Preparation C. Each of these preparations was divided into small portions and one portion (two portions for Preparation B) placed in each of several desiccators conditioned at 11, 32, 42, 58, 66, 84 and 100 per cent R.H. Conditioning time in every case was 2 months. One of the portions of Preparation B was removed from each desiccator and placed for two months in 11 per cent R.H.; this was designated Series B(R). The different groups of DTA runs were labelled Series A, B, C and B(R) as previously shown.

Thermal analysis

In this work, DTA and TGA of samples prepared as previously described were carried out under controlled conditions of humidity. The details have been published elsewhere. (3) Normal TGA runs were performed at a heating rate of $10^{\circ}\text{C}/\text{min}$ under vacuum. Static runs were also performed by heating at 100° for 3 hr under vacuum. Samples were compacted at 5000 psi to prevent blowing and loss of powder during evacuation and heating. In the DTA runs, the cell was placed in a gloved box controlled at the required humidity. In each experiment 16 mg of the sample were weighed in a balance placed in the gloved box. Aluminum cups were used as sample holders and the remote DTA cell supplied by DuPont Co. was adopted for this work. Thermal curves were obtained at heating rates of 10 and $20^{\circ}\text{C}/\text{min}$.

Determination of Free CaO and CO_2

Free lime was determined by the solvent variation method (SVM) (4).

The actual amount of $\text{Ca}(\text{OH})_2$ was determined by taking into account that which had reacted with CO_2 to form CaCO_3 and that which had dissolved in the water during bottle hydration.

CO_2 was determined by adding sulfuric acid to the sample and absorbing the evolved CO_2 in $\text{Ba}(\text{OH})_2$. Excess $\text{Ba}(\text{OH})_2$ was estimated by titrating with HCl. The experiment was carried out in a closed system.

Results and Discussion

(i) State of Water - Water Content - Relative Humidity Relationships

As was found previously for hydrated portland cement (3) the dynamic TGA did not show as clear a delineation of different types of water as the DTA curves. However, under static conditions, heating in vacuum at 100°C for 3 hours gives a condition approximately equivalent to the d-dry condition so that quantitative information could be obtained and related to the intensity of the DTA curves of each sample. In addition sorption and partial scanning isotherms (5) can be constructed by determining the amount of water held in each of the samples exposed to the different humidity conditions by the static TGA described previously. Equilibrium at each point is assured due to the lengthy periods allowed for it to be attained. These results are presented in Figure 1.

The outer boundary sorption curve is obtained from the samples of Series B, and the approximate scanning curves, dotted lines, are drawn in from the points obtained on returning each point to 11 per cent R.H., Series B(R). Preparation C, Series C represents the outer boundary desorption curve. The slope of this curve, in the low humidity region from 42 to 11 per cent R.H., is much greater than the slope of the scanning curves and that of the readsorption curve obtained from readsorption on Preparation A, Series A. This cannot be explained by capillary condensed water in Preparation C. Series A has the same slope as the scanning curves up to about 60 per cent R.H. It is pertinent that the sample of Series B(R) which had been

exposed to 100 per cent R.H. has almost reattained the water content of the original Preparation A at 11 per cent R.H. In other words most of the inter-

FIG. 1

Sorption isotherm of bottle hydrated C_3S

layer water has returned to the sample of Preparation B(R); in addition, it is clear from the scanning curves that this return of interlayer water takes place over the full range as the sample is exposed to different humidities thus invalidating the use of these curves for BET surface area calculations. The phenomenon of the scanning curves was also observed for hydrated portland cement (5) but there was a possibility that rehydration of some calcium sulphoaluminate or other aluminates might be partly responsible for this. These results on hydrated C_3S clearly show that scanning curves owe their origin to the C-S-H phase.

The low slope of the curve representing readsorption of Preparation A (Series A), compared to the outer boundary desorption (Series C) curve indicates that some dissociation of a hydrate occurs above the 11 per cent R. H. level during drying of Preparation C most of which recombines above 66 per cent R.H. on rewetting (Series A). In this work, however, an attempt was made to obtain the stoichiometry of the hydrate only at the 11 per cent R.H. level on the outer boundary desorption curve (Preparation A), for reasons mentioned above. The hysteresis shown here between the adsorption and desorption curves is similar quantitatively and qualitatively to that of Helmuth (6) and contrary to that of Hagymassy (7). This work thus verifies the existence of scanning loops and the secondary hysteresis, and confirms that this is a property of the calcium silicate hydrate. Previous work (1, 3, 5) on cement has shown that the hysteresis is due to rehydration of the d-dried material.

(ii) State of Water - Differential Thermal Analysis

Results for Series A, B and C for a heating rate of $10^{\circ}\text{C}/\text{min}$ are presented on Figure 2. Series B, the d-dried sample, shows a simultaneous growth of two endothermic peaks at 75° and 110°C probably due to adsorbed and interlayer water respectively. The peak at 110°C is first of higher intensity but at higher humidities the 75°C peak exceeds it and a general merging of the peaks occurs from 66 per cent R.H. There is evidence for other endothermal effects at approximately 200 and 300°C but, due to severe baseline shifting in this temperature range, it cannot be clearly seen. This is

FIG. 2

DTA thermograms at $10^{\circ}\text{C}/\text{min}$ (a) Series A
(b) Series B (c) Series C

more clearly observed when the heating rate is $20^{\circ}\text{C}/\text{min}$ as shown on Figure 3 Series (B) although the peaks have shifted to higher temperatures relative to $10^{\circ}\text{C}/\text{min}$. These peaks are probably due to decomposition of hydroxyl groups within the silicate. The peaks tend to merge at the higher humidities. Figure 2 Series (A) presents the DTA traces of the original material, Preparation A, which has been equilibrated at 11 per cent R.H. The trace at 11 per cent R.H. shows a much larger peak at 110°C than the trace for the d-dried Series (B) at 11 per cent R.H. This is because the latter does not contain as much interlayer water at this humidity since it has been d-dried.

Series (A) shows the low temperature peak at 75°C representing adsorbed water growing largely by itself until it has merged with the other peaks at the high humidities. At each humidity above 42 per cent R.H. the intensity of the 75°C peak for Series (A) clearly exceeds that of Series (B). This is perhaps due to the fact that Series (A) has not been d-dried and probably has a higher surface area than the d-dried sample Series (B).

Series (C), the outer boundary desorption curve, shows the feature observed from the isotherm that, at each humidity, more water is present than for Series (A). The peaks, however, are generally merged and little can be learned concerning the relative size of the peaks.

DTA curves for Series B(R), in which samples exposed to various humidities have all been returned to 11 per cent R.H., are shown on Figure 3. It is clear from the first curve that the first peak is very small, while the second peak is relatively large. Each curve exhibits an increase in the second peak, (except possibly at 100 per cent and 84 per cent R.H.) and thus confirms the gravimetric results, (Figure 1), the results obtained by several techniques for hydrated cement, and the non-unique nature of the 11 per cent R.H. condition and the change in peak area (Figure 3, Series B(R)). Eleven per cent to 32 per cent to 42 per cent R.H. exposure conditions again confirm the fact that interlayer water is re-entering at the lower humidities; despite a long conditioning period the nonreversibility at low humidities is apparent. This invalidates the use of H_2O as an adsorbate for surface area measurements for this system. Comparing Series B(R) Figure 3, with Series (A) Figure 2 (sample was not d-dried) where the lower temperature peak, alone, grows with the increasing humidity, and Series (B) Figure 2, (sample was d-dried) where both peaks grow, emphasizes the point on interlayer re-entry, i.e., at high humidities most of the water has re-entered.

(iii) Hydrates Beyond the D-Dried State

Making the reasonable assumption for a type II isotherm that at 11 per cent R.H., on the outer boundary sorption curve (Series B), one molecular layer of adsorbed water exists on the free surface of the d-dried material, one may estimate how much hydrate water is associated with the

sample at this humidity after the sample has been exposed to 100 per cent R.H. Much work, (8, 9) involving helium flow techniques has shown that at 11 per cent R.H. a large portion of the sorbed water re-enters the interlayer structure.

The surface area, measured by nitrogen, of the d-dried material is $70.3 \text{ m}^2/\text{gm}$ which corresponds to 1.93 per cent of water to cover the surface with one monolayer assuming one molecule of H_2O covers $10.8\text{\AA}^2$. After exposure to 100 per cent R.H. and redrying to 11 per cent R.H., the sample contains 6.87 per cent of water above the d-dried position. Assuming the surface area is unchanged by rewetting and second

FIG. 3

DTA thermograms for
(a) Series B at 20°C/min
(b) Series B(R) at 10°C/min

drying, this leaves $6.87 - 1.93 = 4.94$ per cent of water as a higher hydrate; this is equivalent to 5.98 per cent on the ignited basis and converts to 1.52 moles of higher hydrate water associated in the reaction with two moles of C_3S .

(iv) The Over-all Stoichiometry of the Reaction

The loss in weight on ignition of the hydrated C_3S conditioned at 11 per cent R.H. is 29.61 per cent of the ignited weight. Correction for the decomposition of the carbonate results in the loss being 28.54 per cent. From 11 per cent R.H. to the d-dry position, 8.33 per cent of the ignited weight (6.87 on d-dry basis, Figure 1) is lost so that the weight loss from the d-dry state to the ignited state is 20.21 per cent, or 0.2021 g H_2O /gm C_3S . This value compares well with that given by other authors, (10, 11) and corresponds to 2.56 moles H_2O /mole C_3S reacted up to the reference of the d-dry state or 5.12 moles H_2O /2 moles C_3S . Taking the additional constitutional water at the 11 per cent R.H. into account results in a total of 6.64 moles H_2O combining with 2 moles C_3S .

The estimation of free lime is necessary for the establishment of the CaO/SiO_2 as well as the reaction equation, since from it, one also determines the lime and water content associated with the silicate hydrate. In this work the well-known SVM method (4) was used as it is shown to give fairly accurate results. The value obtained after corrections for carbonation was 33.41 per cent, yielding a value of 1.64 for CaO/SiO_2 ratio of the hydrated silicate. This value approximates the higher values obtained by Locher (10) for C_3S pastes at high water-cement ratios.

The equation for the reaction using the d-dried reference condition may be written thus:

The difference between the CaO/SiO_2 and H_2O/SiO_2 of the d-dried hydrated silicate is thus 0.44 which again is similar to the value determined by other workers (10, 11). The equation for the condition at 11 per cent R.H. on drying from 100 per cent R.H. may be written as follows:

This yields a value for $CaO/SiO_2 - H_2O/SiO_2$ of -0.32 with a H_2O/SiO_2 of 1.96. If the stoichiometry of the hydrate was measured at higher humidities the excess of H_2O/SiO_2 over CaO/SiO_2 might be even greater. The usual

assumption is that there are 3 moles of water in the silicate hydrate, and a $\text{H}_2\text{O}/\text{SiO}_2$ of 1.50, one of the three molecules of water, residing between the sheets. At the 11 per cent R.H. condition, it appears that 1.52 moles may exist between the sheets and more at higher humidities.

Conclusions

The condition at 11 per cent R.H. (drying from 100 per cent R.H.) is a good base for studying the stoichiometry of calcium silicate hydrate. The stoichiometry of the bottle-hydrated C-S-H gel at 11 per cent R.H. approached from 100 per cent R.H. is $3.28 \text{ CaO} : 2\text{SiO}_2 : 3.92\text{H}_2\text{O}$. Results suggest that at higher humidities, higher hydrates may exist.

Interlayer water re-enters the d-dried C-S-H structure below 11 per cent R.H. and throughout the humidity range. At the 100 per cent R.H. exposure, almost complete re-entry seems to occur.

When specimens are dried from 100 to 10 per cent R.H. dehydration occurs. This is very evident at humidities of 40 per cent and lower, but might even occur between 100 and 40 per cent; this could not be ascertained because of capillary condensation in this region.

Thermograms delineate the free and interlayer water and their relative intensities for samples exposed to different conditions show a good relationship with the adsorption isotherms.

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STOICHIOMETRY, TRICALCIUM SILICATE, BOTTLE HYDRATION

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