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Validity of Using Methanol for Studying the Microstructure of Cement Paste

by J.J. Beaudoin

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RÉSUMÉ

On a effectué des essais afin de déterminer l'importance de l'interaction du méthanol et de l'hydroxide de calcium à 22° C. On a utilisé les techniques suivantes : diffraction aux rayons X, spectroscopie infrarouge, détermination de l'aire superficielle, variation de longueur, calorimétrie, analyse thermique différentielle et thermogravimétrie. On en a conclu que du méthylate de calcium ou un composé méthylé se forme lorsqu'on mélange de l'hydroxide de calcium avec du méthanol.

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Validity of using methanol for studying the microstructure of cement paste

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Experiments were conducted to assess the extent of interaction of methanol with calcium hydroxide at 22° C. The following techniques were used: X-ray diffraction, infrared spectroscopy, surface-area determination, length change, calorimetry, differential thermal analysis and thermogravimetric analysis. It was concluded that either calcium methoxide or a methylated complex is formed when calcium hydroxide is mixed with methanol.

1. INTRODUCTION

The effect of calcium hydroxide (Ca(OH)_2), constituting 26% by volume of cement paste, on the microstructure and mechanical properties of cement paste is not completely understood. Some studies suggest that Ca(OH)_2 has good engineering properties and affects the mechanical behaviour of cement paste [1].

Several studies of the microstructure of cement paste describe solvent replacement with methanol (CH_3OH) as a technique that preserves the "wet state" structure of the material; for example, large decreases in the nitrogen surface area do not result in removal of CH_3OH [2,3]. An implicit assumption in these studies is that the solvent does not interact with C-S-H or Ca(OH)_2 , but recent work has indicated that this assumption is incorrect [4].

Opinions differ as to the nature of the CH_3OH - Ca(OH)_2 interaction. The suggestion that CH_3OH reacts with Ca(OH)_2 to form calcium methoxide ($\text{Ca(OCH}_3)_2$) or a carbonate-like product [5] has not been accepted by all investigators [3,6]. It was of interest to establish the nature of the solvent- Ca(OH)_2 interaction, as non-aqueous media are often used to characterize cement systems. The results of applying several techniques to the CH_3OH - Ca(OH)_2 system are discussed.

2. EXPERIMENTAL

2.1 Materials

Calcium hydroxide (Ca(OH)_2): reagent-grade powder with a surface area of $12.0 \times 10^3 \text{ m}^2 \text{ kg}^{-1}$. Alcohols: reagent-grade methyl, ethyl and other aliphatic alcohols. Calcium methoxide ($\text{Ca(OCH}_3)_2$): surface area of $60 \times 10^3 \text{ m}^2 \text{ kg}^{-1}$. This material, for which the XRD and IR spectra matched published spectra [7], was prepared according to procedures described by Robinson and Scott [8].

2.2 Specimens

Ca(OH)_2 was used in both compacted and powder form. Powder was compacted at pressures of 345 and 690 MPa to produce circular disks 32 mm in diameter and 1.27 mm thick. To study the interaction of alcohol with Ca(OH)_2 powder, both substances were placed in 100-ml glass bottles and stirred continuously. The ratio of liquid to solids by volume was 5 to 1.

2.3 Surface area measurement

Nitrogen surface area measurements were obtained with a Quantasorb surface area analyser.

2.4 Length change

Modified Tuckerman optical extensometers with a sensitivity of $4 \times 10^{-6} \text{ mm mm}^{-1}$ were used.

2.5 X-ray diffraction

X-ray diffraction data were obtained with a Guinier-Hägg powder camera, Model XDC-700.

2.6 IR spectroscopy

A Nicolet model 6000 fourier transform IR spectrometer with a mercury-cadmium-telluride detector was used, which had a resolution of 4 cm^{-1} . Computation conditions included one level of zero filling and Happ Genzel apodization.

2.7 Thermal analysis

DTA and TGA were carried out using a 1090 Dupont Thermal Analyzer containing a 951 TGA accessory. Both air and nitrogen atmospheres were used. Generally, 20-mg samples were heated at $20^\circ \text{C min}^{-1}$.

2.8 Conduction calorimetry

The rate and amount of heat development in CH_3OH - Ca(OH)_2 mixtures were measured using a conduction calorimeter. The calorimeter, supplied by the Institute

of Applied Physics, Delft, Holland, has been described previously [9]. For data acquisition and processing, the calorimeter was interfaced with an Apple IIe using a Taurus One 12-bit analog-to-digital converter, and an Apple super-serial interface card.

3. RESULTS AND DISCUSSION

3.1 X-ray diffraction

Both powdered and compacted samples of $\text{Ca}(\text{OH})_2$ were submerged in CH_3OH for 24 h, dried by pumping *in vacuo* for 8 h, and prepared for X-ray diffraction measurements. New peaks were observed at d -spacings of 0.834, 0.419, 0.291, 0.277 and 0.176 nm. It has been suggested that $\text{Ca}(\text{OCH}_3)_2$ is a possible reaction product of a CH_3OH - $\text{Ca}(\text{OH})_2$ interaction [5]. The observed spacings corresponded to those assigned to $\text{Ca}(\text{OCH}_3)_2$ with the spacing at 0.834 nm being very strong. The X-ray pattern, however, did not include the d -spacings for $\text{Ca}(\text{OCH}_3)_2$ at 0.316 and 0.184 nm. $\text{Ca}(\text{OCH}_3)_2$ was also prepared; the d -spacings matched those given in the JCPDS card file.

Fig. 1 Infrared spectra: $\text{Ca}(\text{OH})_2$; $\text{Ca}(\text{OCH}_3)_2$; $\text{Ca}(\text{OH})_2 + \text{CH}_3\text{OH}$ interacted for 2 h, 1 day.

3.2 Infrared spectroscopy

Infrared spectra of $\text{Ca}(\text{OH})_2$, $\text{Ca}(\text{OCH}_3)_2$ and the product from the $\text{Ca}(\text{OH})_2$ - CH_3OH interaction are given in fig. 1. Two samples of the $\text{Ca}(\text{OH})_2$ - CH_3OH system were obtained by mixing $\text{Ca}(\text{OH})_2$ powder in CH_3OH for 2 and 24 h. The samples were dried by pumping *in vacuo* for 8 h. Free CH_3OH was not detected in either sample, as concluded from the absence of peaks at 3337 and 1021 cm^{-1} . The 2-h sample had wavenumbers at 3640, 3408, 2591, 1788, 1450, 1098 and 865 cm^{-1} . These peaks were due to the presence of unreacted $\text{Ca}(\text{OH})_2$ and what appeared to be early formation of $\text{Ca}(\text{OCH}_3)_2$. In addition, the 24-h sample had wavenumbers at 2922, 2837, 2778 and 2098 cm^{-1} . These bands were similar to those present in the IR spectra of $\text{Ca}(\text{OCH}_3)_2$. Although mixed or poor crystallinity could account for some discrepancy with published spectra, the evidence indicated that a new reaction product was formed.

3.3 Surface area

Nitrogen surface areas were determined for $\text{Ca}(\text{OH})_2$ samples immersed in CH_3OH for different periods (fig. 2). The surface area of $\text{Ca}(\text{OH})_2$ increased from 13.2×10^3 to $29.4 \times 10^3 \text{ m}^2 \text{ kg}^{-1}$ in 4 h. Apparently, reaction products with a surface area larger than that of $\text{Ca}(\text{OH})_2$ were formed. As previously stated, formation of $\text{Ca}(\text{OCH}_3)_2$ has been suggested. Using the value $60 \times 10^3 \text{ m}^2 \text{ kg}^{-1}$ as the surface area of $\text{Ca}(\text{OCH}_3)_2$, it was estimated that about 29.0% $\text{Ca}(\text{OH})_2$ reacted at 4 h. It is not clear why there was little change in the surface area after 4 h. Possibly, N_2 was excluded from the surface that became inaccessible during drying because of ageing or agglomeration effects. However, evidence from thermal analysis (to be presented later) indicated the reaction did not cease at 4 h.

Fig. 2 Nitrogen surface area of $\text{Ca}(\text{OH})_2$ samples immersed in methanol for different periods.

Increases in the surface area of Ca(OH)_2 samples immersed in other aliphatic alcohols were much smaller. Surface areas increased from $13.2 \times 10^3 \text{ m}^2 \text{ kg}^{-1}$ to 15.47, 14.66, $13.67 \times 10^3 \text{ m}^2 \text{ kg}^{-1}$ in samples treated with ethyl, amyl and butyl alcohol, respectively.

3.4 Length change

The length change of compacted samples of Ca(OH)_2 (formed at 345 MPa) immersed in CH_3OH and ethanol is plotted in fig. 3. Length change of the samples was much greater in CH_3OH , increasing to 0.27% after 45 h. The length change in ethanol was small, increasing to only 0.02% after 20 h. The length change of Ca(OH)_2 in water (not shown) was about 0.2%. The large length change in CH_3OH may have been due to several factors. The formation of $\text{Ca(OCH}_3)_2$ results in the release of water as a reaction product. This water may interact with unreacted Ca(OH)_2 , thereby contributing to the length change. The length change of Ca(OH)_2 in water is attributed to physical adsorption at low humidities, and dissolution and recrystallization at points of solid contact when the humidity is higher [10].

Fig. 3 Length change of calcium hydroxide compacts immersed in methanol and ethanol.

Expansion may also be caused by pressure resulting from the increase in specific volume of the reaction products; for example, $\text{Ca(OCH}_3)_2$ has a specific volume of 0.575 cc g^{-1} . The larger surface area of the reaction products would also result in increased length change due to physical adsorption. Another factor may be the release of strain energy from the Ca(OH)_2 particles after interaction with CH_3OH ; if so, the small length change in ethanol suggests that there is little interaction between ethanol and Ca(OH)_2 .

3.5 Conduction calorimetry

Heat evolution *versus* time curves for CH_3OH and ethanol plus Ca(OH)_2 , and CH_3OH plus calcium carbonate, are plotted in fig. 4. In each test, 10 ml of

Fig. 4 Heat evolved *versus* time curves – (1) methanol, and (2) ethanol, plus calcium hydroxide; (3) methanol plus calcium carbonate.

solvent was mixed with 5 g of sample. The test temperature was $25 \pm 0.001^\circ \text{C}$. The heat developed in the $\text{CH}_3\text{OH}-\text{Ca(OH)}_2$ system was much greater than in the other two systems and even exceeded the heat of dissolution in the $\text{Ca(OH)}_2-\text{H}_2\text{O}$ system (not shown). The amount of heat developed in the CH_3OH -calcium-carbonate and CH_3OH -titanium-oxide (not shown) systems was similar and consisted primarily of heats of stirring and wetting. Surface areas of the solids in all four systems were similar. The greater heat developed in the $\text{CH}_3\text{OH}-\text{Ca(OH)}_2$ system may have been the result of a chemical interaction.

3.6 Thermal analysis

DTA experiments were conducted (in air and nitrogen) on CH_3OH -treated Ca(OH)_2 samples to determine whether a reaction between CH_3OH and Ca(OH)_2 had occurred. Curves for experiments conducted in air are presented in fig. 5. The first curve for Ca(OH)_2 has a large endotherm at about 500°C . A small amount of carbonation is evident from the endothermic peak at 720°C .

In the second curve in fig. 5, which is for the CH_3OH -treated Ca(OH)_2 system (3-day interaction time), there are large exothermic peaks at 330 and 450°C . Other curves for this system (not shown) obtained at different interaction times exhibit exothermic peaks at 370, 400 and 485°C . The intensity and position of the peaks are dependent on interaction time. It is difficult to assign these exothermic peaks to $\text{Ca(OCH}_3)_2$ because $\text{Ca(OCH}_3)_2$ interacts with Ca(OH)_2 during a DTA cycle.

A set of TGA curves (not given) was obtained for samples of Ca(OH)_2 that were mixed with CH_3OH for increasing lengths of time. Weight loss at 600 to 800°C in air for these $\text{Ca(OH)}_2-\text{CH}_3\text{OH}$ preparations is plotted against reaction time in fig. 6. The increase in weight loss from 3.2% to more than 20% after 12 h confirms the findings of Day, who suggested the formation of a "carbonate-like" product [5]. The carbonate-like product is actually CaCO_3 formed from the

Fig. 5 DTA curves (in air) for (a) Ca(OH)_2 and (b) $\text{Ca(OH)}_2 + \text{CH}_3\text{OH}$ interacted for 3 days.

Fig. 6 Weight loss due to decomposition of CaCO_3 formed during TGA of samples produced by interacting Ca(OH)_2 and methanol for different time periods.

decomposition of the reaction products. Weight loss at 600 to 800°C for the Ca(OH)_2 - $\text{Ca(OCH}_3)_2$ mixtures heated in air increased with the amount of Ca(OH)_2 in the mixture. In nitrogen, weight loss was maximum for mixtures with equal parts of $\text{Ca(OCH}_3)_2$ and Ca(OH)_2 . It appears that CO_2 liberated on the decomposition of $\text{Ca(OCH}_3)_2$ may form additional CaCO_3 by reacting with Ca(OH)_2 . The amount of carbonate formed would depend on the mixture proportions.

4. CONCLUSIONS

The following conclusions may be drawn from this study:

1. Evidence provided by several techniques (XRD, IRS, calorimetry, length change, surface area measurement, DTA and TGA) supports the hypothesis that CH_3OH reacts with Ca(OH)_2 at 22°C.

2. Similarities between the reaction products and $\text{Ca(OCH}_3)_2$ were detected by the above techniques. It is concluded that either $\text{Ca(OCH}_3)_2$ or a methylated complex is formed when Ca(OH)_2 is mixed with CH_3OH .

3. The implications of a CH_3OH - Ca(OH)_2 interaction should be considered in the development of test methods for concrete that employ CH_3OH .

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RESUME

L'utilisation du méthanol pour étudier la microstructure de la pâte de ciment est-elle valable?

On a exécuté des essais afin de déterminer l'importance de l'interaction du méthanol et de l'hydroxide de calcium à 22° C. On a utilisé les techniques suivantes: diffraction X, spectroscopie infrarouge, détermination de l'aire superficielle, variation de longueur, analyse thermique différentielle et thermogravimétrie. Les résultats de ces essais ont mis en évidence la formation d'un produit nouveau. On a observé la présence de méthylate de calcium dans le diagramme X d'hydroxide de calcium traité au méthanol. Pour ce système, les pics IR correspondaient aussi à ceux qui se trouvaient dans le spectre IR du méthylate de calcium. On a observé des augmentations importantes de l'aire superficielle mesurée par

absorption d'azote et la variation de longueur d'échantillons d'hydroxide de calcium après traitement au méthanol. En outre, on a observé une interaction chimique entre le méthanol et l'hydroxide de calcium mise en évidence par les courbes évolution thermique en fonction du temps obtenues par calorimétrie différentielle. Des pics exothermiques de 330 et 450° C dans les courbes ATD d'hydroxide de calcium traité au méthanol indiquait la formation d'un nouveau composé. Les données ATG ont montré une augmentation en rapport avec le temps de la perte de poids (600 à 800° C) correspondant à la décomposition du carbonate de calcium qui résulte de la formation et de la décomposition du méthylate de calcium.

Il faut considérer les implications de l'interaction méthanol-hydroxide de calcium dans le développement des méthodes d'essai pour le béton qui utilisent le méthanol.

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