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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 ( $\text{Ca}(\text{OH})_2$ ), constituting 26% by volume of cement paste, on the microstructure and mechanical properties of cement paste is not completely understood. Some studies suggest that  $\text{Ca}(\text{OH})_2$  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 ( $\text{CH}_3\text{OH}$ ) 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  $\text{CH}_3\text{OH}$  [2,3]. An implicit assumption in these studies is that the solvent does not interact with C-S-H or  $\text{Ca}(\text{OH})_2$ , but recent work has indicated that this assumption is incorrect [4].

Opinions differ as to the nature of the  $\text{CH}_3\text{OH}$ - $\text{Ca}(\text{OH})_2$  interaction. The suggestion that  $\text{CH}_3\text{OH}$  reacts with  $\text{Ca}(\text{OH})_2$  to form calcium methoxide ( $\text{Ca}(\text{OCH}_3)_2$ ) 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- $\text{Ca}(\text{OH})_2$  interaction, as non-aqueous media are often used to characterize cement systems. The results of applying several techniques to the  $\text{CH}_3\text{OH}$ - $\text{Ca}(\text{OH})_2$  system are discussed.

## 2. EXPERIMENTAL

### 2.1 Materials

Calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ): 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 ( $\text{Ca}(\text{OCH}_3)_2$ ): 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

$\text{Ca}(\text{OH})_2$  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  $\text{Ca}(\text{OH})_2$  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  $4 \text{ cm}^{-1}$ . 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  $\text{CH}_3\text{OH}$ - $\text{Ca}(\text{OH})_2$  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  $\text{CH}_3\text{OH}$  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  $\text{CH}_3\text{OH}-\text{Ca}(\text{OH})_2$  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.

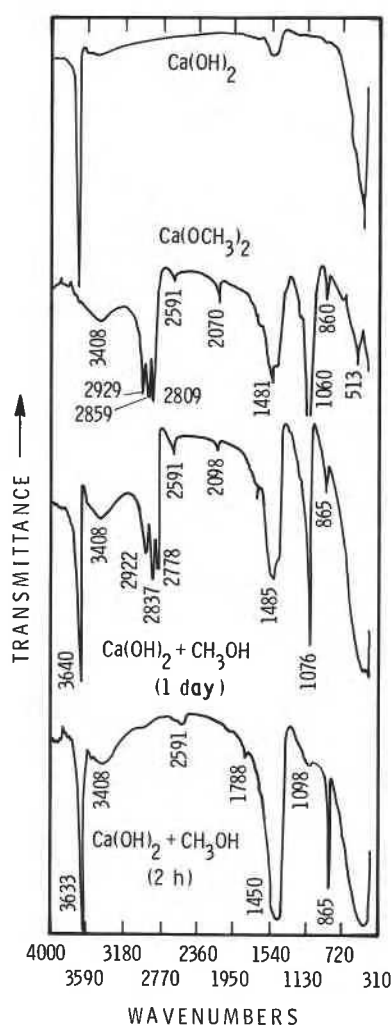


Fig. 1 Infrared spectra:  $\text{Ca}(\text{OH})_2$ ;  $\text{Ca}(\text{OCH}_3)_2$ ;  $\text{Ca}(\text{OH})_2 + \text{CH}_3\text{OH}$  interacted for 2 h, 1 day.

#### 3.2 Infrared spectroscopy

Infrared spectra of  $\text{Ca}(\text{OH})_2$ ,  $\text{Ca}(\text{OCH}_3)_2$  and the product from the  $\text{Ca}(\text{OH})_2-\text{CH}_3\text{OH}$  interaction are given in fig. 1. Two samples of the  $\text{Ca}(\text{OH})_2-\text{CH}_3\text{OH}$  system were obtained by mixing  $\text{Ca}(\text{OH})_2$  powder in  $\text{CH}_3\text{OH}$  for 2 and 24 h. The samples were dried by pumping *in vacuo* for 8 h. Free  $\text{CH}_3\text{OH}$  was not detected in either sample, as concluded from the absence of peaks at 3337 and 1021  $\text{cm}^{-1}$ . The 2-h sample had wavenumbers at 3640, 3408, 2591, 1788, 1450, 1098 and 865  $\text{cm}^{-1}$ . 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  $\text{cm}^{-1}$ . 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  $\text{CH}_3\text{OH}$  for different periods (fig. 2). The surface area of  $\text{Ca}(\text{OH})_2$  increased from  $13.2 \times 10^3$  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,  $\text{N}_2$  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.

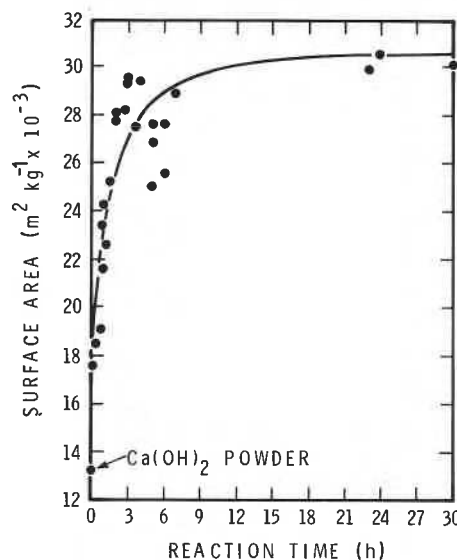


Fig. 2 Nitrogen surface area of  $\text{Ca}(\text{OH})_2$  samples immersed in methanol for different periods.

Increases in the surface area of  $\text{Ca}(\text{OH})_2$  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  $\text{Ca}(\text{OH})_2$  (formed at 345 MPa) immersed in  $\text{CH}_3\text{OH}$  and ethanol is plotted in fig. 3. Length change of the samples was much greater in  $\text{CH}_3\text{OH}$ , 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  $\text{Ca}(\text{OH})_2$  in water (not shown) was about 0.2%. The large length change in  $\text{CH}_3\text{OH}$  may have been due to several factors. The formation of  $\text{Ca}(\text{OCH}_3)_2$  results in the release of water as a reaction product. This water may interact with unreacted  $\text{Ca}(\text{OH})_2$ , thereby contributing to the length change. The length change of  $\text{Ca}(\text{OH})_2$  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].

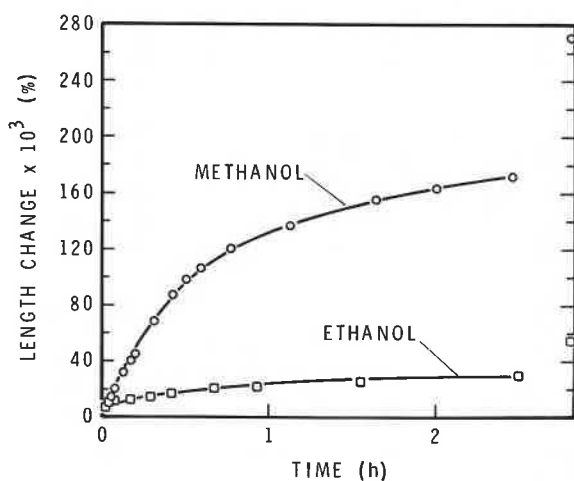


Fig. 3 Length change of calcium hydroxide compacts immersed in methanol and ethanol.

Expansion may also be caused by pressure resulting from the increase in specific volume of the reaction products; for example,  $\text{Ca}(\text{OCH}_3)_2$  has a specific volume of  $0.575 \text{ cc g}^{-1}$ . 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  $\text{Ca}(\text{OH})_2$  particles after interaction with  $\text{CH}_3\text{OH}$ ; if so, the small length change in ethanol suggests that there is little interaction between ethanol and  $\text{Ca}(\text{OH})_2$ .

### 3.5 Conduction calorimetry

Heat evolution *versus* time curves for  $\text{CH}_3\text{OH}$  and ethanol plus  $\text{Ca}(\text{OH})_2$ , and  $\text{CH}_3\text{OH}$  plus calcium carbonate, are plotted in fig. 4. In each test, 10 ml of

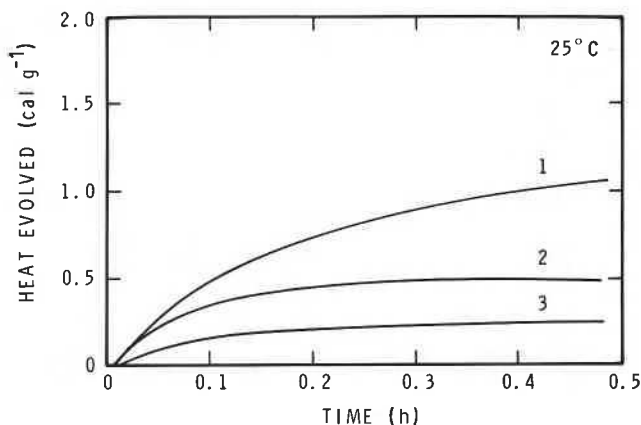


Fig. 4 Heat evolved *versus* time curves – (1) methanol, and (2) ethanol, plus calcium hydroxide; (3) methanol plus calcium carbonate.

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

### 3.6 Thermal analysis

DTA experiments were conducted (in air and nitrogen) on  $\text{CH}_3\text{OH}$ -treated  $\text{Ca}(\text{OH})_2$  samples to determine whether a reaction between  $\text{CH}_3\text{OH}$  and  $\text{Ca}(\text{OH})_2$  had occurred. Curves for experiments conducted in air are presented in fig. 5. The first curve for  $\text{Ca}(\text{OH})_2$  has a large endotherm at about  $500^\circ \text{C}$ . A small amount of carbonation is evident from the endothermal peak at  $720^\circ \text{C}$ .

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

A set of TGA curves (not given) was obtained for samples of  $\text{Ca}(\text{OH})_2$  that were mixed with  $\text{CH}_3\text{OH}$  for increasing lengths of time. Weight loss at  $600$  to  $800^\circ \text{C}$  in air for these  $\text{Ca}(\text{OH})_2-\text{CH}_3\text{OH}$  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  $\text{CaCO}_3$  formed from the

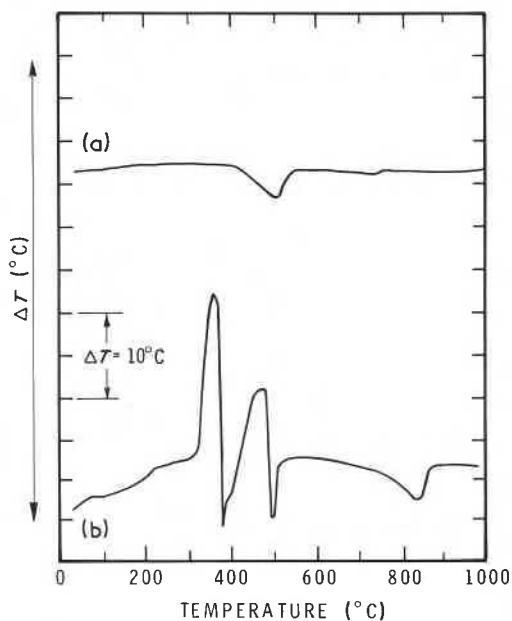


Fig. 5 DTA curves (in air) for (a)  $\text{Ca}(\text{OH})_2$  and (b)  $\text{Ca}(\text{OH})_2 + \text{CH}_3\text{OH}$  interacted for 3 days.

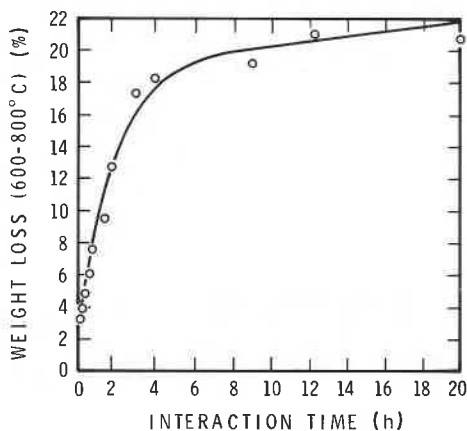


Fig. 6 Weight loss due to decomposition of  $\text{CaCO}_3$  formed during TGA of samples produced by interacting  $\text{Ca}(\text{OH})_2$  and methanol for different time periods.

decomposition of the reaction products. Weight loss at 600 to 800°C for the  $\text{Ca}(\text{OH})_2$ - $\text{Ca}(\text{OCH}_3)_2$  mixtures heated in air increased with the amount of  $\text{Ca}(\text{OH})_2$  in the mixture. In nitrogen, weight loss was maximum for mixtures with equal parts of  $\text{Ca}(\text{OCH}_3)_2$  and  $\text{Ca}(\text{OH})_2$ . It appears that  $\text{CO}_2$  liberated on the decomposition of  $\text{Ca}(\text{OCH}_3)_2$  may form additional  $\text{CaCO}_3$  by reacting with  $\text{Ca}(\text{OH})_2$ . 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  $\text{CH}_3\text{OH}$  reacts with  $\text{Ca}(\text{OH})_2$  at 22°C.

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

3. The implications of a  $\text{CH}_3\text{OH}$ - $\text{Ca}(\text{OH})_2$  interaction should be considered in the development of test methods for concrete that employ  $\text{CH}_3\text{OH}$ .

#### ACKNOWLEDGEMENTS

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#### REFERENCES

1. Beaudoin, J.J., 'A comparison of mechanical properties of compacted calcium hydroxide and portland cement paste systems', *Cem. Concr. Res.* **13** (1983) 319-324.
2. Litvan, G.G., 'Variability of the nitrogen surface area of hydrated cement paste', *ibid.* **6** (1976) 139-144.
3. Parrott, L.J., 'Thermogravimetric and sorption studies of methanol exchange in an alite paste', *ibid.* **13** (1983) 18-22.
4. Beaudoin, J.J., 'Mechanisms of subcritical crack growth in cement paste', Proceedings of International Conference on Fracture Mechanics of Concrete, Lausanne, October 1985.
5. Day, R.L., 'Reactions between methanol and Portland cement paste', *Cem. Concr. Res.* **11** (1981) 341-349.
6. Chandra, S. and Flodin, P., *ibid.* **12** (1982) 261-262.
7. Lutz, H.D., 'IR-spektroskopische und röntgenographische Untersuchungen an  $\text{Mg}(\text{OCH}_3)_2$ ,  $\text{Ca}(\text{OCH}_3)_2$ ,  $\text{Sr}(\text{OCH}_3)_2$  und  $\text{Ba}(\text{OCH}_3)_2$ ', *Z. Anorg. Allgem. Chem.* **353** (1967) 207-215.
8. Robinson, P.L. and Scott, W.E., 'The polysulphides of barium and calcium', *J. Chem. Soc.* (1931) 693-709.
9. Ramachandran, V.S., 'Action of triethanolamine on the hydration of tricalcium aluminate', *Cem. Concr. Res.* **3** (1973) 41-54.
10. Ramachandran, V. S. and Feldman, R. F., 'Length change characteristics of  $\text{Ca}(\text{OH})_2$  compacts on exposure to water vapour', *J. Appl. Chem.* **17** (1967) 328-332.

## 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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