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CARBONATATION OF $Ca(OH)_2$ INVESTIGATED BY THERMAL AND X-RAY DIFFRACTION METHODS OF ANALYSIS

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ETUDE DE LA CARBONATATION DE $Ca(OH)_2$ PAR ANALYSE THERMIQUE ET DIFFRACTION AUX RAYONS X

SOMMAIRE

L'auteur a entrepris une étude nouvelle de la carbonatation de l'hydrate de calcium à l'aide de l'analyse thermique et de la diffraction aux rayons X. La taille des cristaux et la morphologie de $Ca(OH)_2$ varient selon la méthode de préparation, qui affecte également la vitesse et le mécanisme de la réaction de carbonatation. Ces derniers dépendent également de l'état hygrométrique de l'hydrate avant carbonatation. L'auteur décrit l'allure des thermogrammes et étudie la nature des modifications responsables des pointes des courbes.

CARBONATATION OF $Ca(OH)_2$ INVESTIGATED BY THERMAL AND *X*-RAY DIFFRACTION METHODS OF ANALYSIS

By J. E. GILLOTT

The carbonatation of calcium hydroxide has been re-investigated using thermal and *X*-ray diffraction methods of analysis. The crystal size and morphology of $Ca(OH)_2$ vary with the method of preparation, which also affects the rate and mechanism of the carbonatation reaction. This is also dependent upon the relative humidity established prior to carbonatation. The form of the thermograms is described and the nature of the changes responsible for the peaks discussed.

Introduction

Calcium hydroxide is of importance in industry, engineering and agriculture. It was used as a constituent of mortar by the Greeks and Romans and has been employed from early times in agriculture to improve soil tilth. It is of increasing significance in civil engineering practice in the lime stabilisation of soils, and is an important hydration product of Portland cement.

Calcium hydroxide reacts with carbon dioxide to form calcium carbonate. The reaction has been previously investigated in detail.[1,2] It is probably involved in the mechanism by which carbonatation leads to shrinkage of cement[3,4] and in the processes that lead to gain in strength with time, following mixing of lime with soils.[5]

Experimental

Sample preparation

The $Ca(OH)_2$ used in this investigation was prepared by hydration of CaO. It has been known for a considerable time that the properties of CaO are affected by the method of preparation. Time and temperature of firing are of particular importance, though of the two variables, temperature is reported to have the greater effect.[6-8] Lime made by firing at low temperatures is more reactive than lime made at higher temperatures. The high temperature product owes its reduced reactivity to sintering, which gives the material a higher bulk density, reduced porosity, an increased crystallite size and reduced surface area. Differences between samples of CaO may be reflected in differences in the reactivity of the corresponding $Ca(OH)_2$ prepared by hydration. The $Ca(OH)_2$ is also affected by the hydration procedure.

In the present investigation two stocks of CaO were prepared. Analytical reagent grade $Ca(OH)_2$ was fired for 16 h at temperatures of 500° and 1100°.

Three methods were employed for the preparation of $Ca(OH)_2$. CaO was hydrated in distilled water, in vapour phase at 22°, and in vapour phase at 100°. Vapour-phase hydration was carried out at relative humidities of 25 and 97% obtained by use of saturated salt solutions or mixtures of water and sulphuric acid.

All samples of $Ca(OH)_2$ were allowed to come to equilibrium at a relative humidity of either 25 or 97% prior to carbonatation. This was carried out in a CO_2 atmosphere, and samples were removed after increasing time intervals and stored in a desiccator for analysis.

Analytical procedure

Samples were analysed by *X*-ray diffraction and thermal methods. Some were examined microscopically on the petrographic and electron microscopes. *X*-ray diffraction powder photographs were taken with a Nonius Guinier quadruple-focussing camera employing monochromatic copper radiation. A Hilger diffractometer with furnace attachment was also employed. Differential thermal analysis (D.T.A.) was carried out in a nitrogen or steam atmosphere on an R. L. Stone Co. apparatus using the dynamic gas system of sample atmosphere control. Reduced pressure was employed in certain of the differential thermal analyses. A silica spiral and Cahn thermal balance were used to observe weight changes on heating.

Results

X-ray diffraction and D.T.A. showed that samples of CaO made by firing for 16 h at 500° contained a small amount of calcite, and weak broad lines on the *X*-ray powder pattern showed that dehydroxylation of the $Ca(OH)_2$ was not complete. The samples of CaO made by firing at 1100° did not contain $Ca(OH)_2$ and there were only weak indications of calcite.

X-ray analysis was employed to determine whether formation of $Ca(OH)_2$ by all three methods of hydration of the CaO had gone to completion. Samples of $Ca(OH)_2$ prepared by vapour-phase hydration showed conspicuous broadening of *X*-ray diffraction powder lines. This may have resulted from small crystallite size, imperfections in the crystals, or both. The $Ca(OH)_2$ made by water hydration gave sharper *X*-ray powder lines. These samples were dispersed in trichloroethylene using an ultra-sonic bath and examined on the electron microscope. The crystals prepared by water hydration display needle- or lath-like forms and have long dimensions of about 2500 Å (0·25 μ) (Fig. 1a). The $Ca(OH)_2$ made by vapour hydration occurs as small plate-like crystals of about 250 Å dia. This agrees with the dimension deduced from an approximate analysis of the *X*-ray line broadening. The crystal platelets are surrounded by and enclosed within what appears to be amorphous material (Fig. 1b). The suggestion has been made that vapour-phase hydration involves a topochemical reaction, whereas hydration in liquid water may involve a 'through solution and crystallisation' process.[9]

Thermograms of samples which had been exposed to CO_2 (pre-carbonatated samples) showed three or four major peaks, depending on the conditions. Thermal analysis showed that in general, samples hydrated in vapour phase at 22 and 100° behaved similarly on carbonatation whereas water-hydrated samples behaved differently.

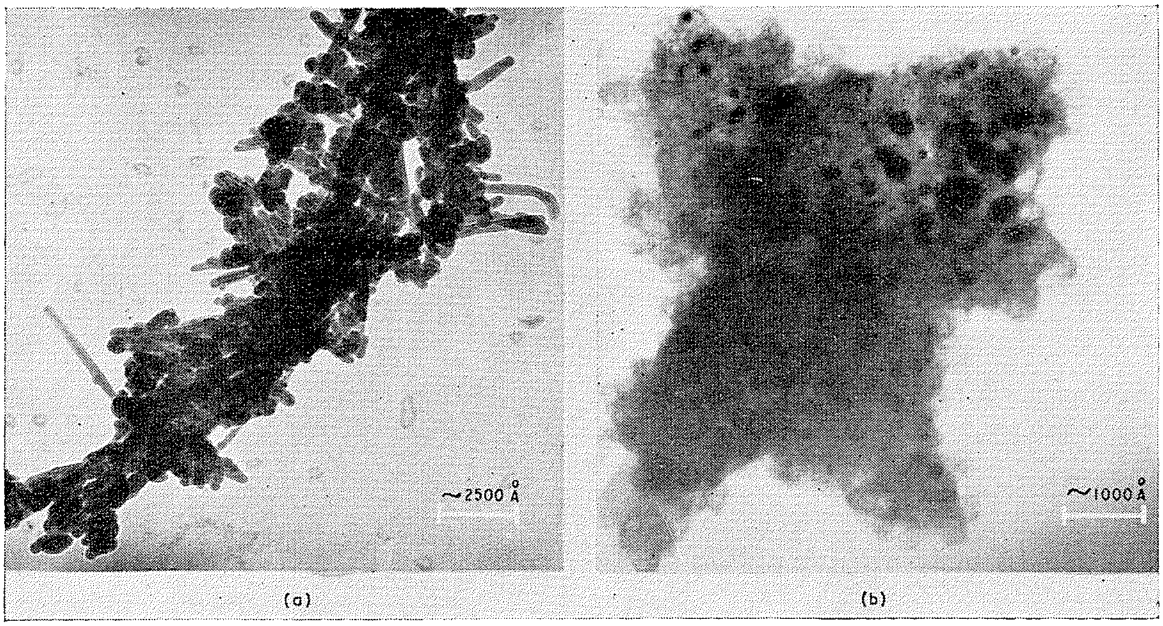

Fig. 1. *Electron micrographs of* $Ca(OH)_2$
(a) Water hydrated
(b) Vapour hydrated at 22°

A small endothermic peak at about 250° was detected on many of the thermograms. Samples made by vapour-phase hydration at either 22 or 100° and carbonatated after conditioning to 25% R.H. showed a sharp exotherm at 300° to 310°. On samples prepared by water hydration and conditioned at 25% R.H. prior to carbonatation, this peak was present *only* on thermograms of samples treated in CO_2 for 1 h or less. Such material treated in CO_2 for longer periods did not display this peak on the thermogram (Fig. 2). The peak was absent on all but one of the samples carbonatated at 97% R.H.

An endothermic peak was present between 400 and 500° on all samples except those in which carbonatation had gone to virtual completion. The peak was double on certain of the water-hydrated samples (e.g. 4 days CO_2, 97% R.H., 1100° in Fig. 2), some of which were subjected to D.T.A. under a reduced pressure of about 8 mm Hg. Under these conditions a sharp peak at about 415° was recorded and an improved resolution of the subsidiary peaks obtained. A peak was registered at about 490° and a small inflection at about 425°. Analyses were also carried out in a steam atmosphere. The peak system normally found in the 400° to 500° temperature range was shifted to a temperature of about 545°, but the multiple peak system showed only as a slight inflection on the low temperature side of a single endothermic peak.

An endothermic peak, the size of which depended on the extent of carbonatation, was recorded at a temperature in excess of 600°. It was occasionally double and a peak occurred at about 590°, followed by another at about 650°. It was found in some cases that after the material had been stored under vacuum for several days the peak at 590° was not registered and only that at about 650° was recorded.

A weight-loss curve was recorded by means of the Cahn thermal balance from a sample of water-hydrated $Ca(OH)_2$ carbonatated for four days at 97% R.H. Significant changes in weight were registered over several temperature ranges. A sharp inflection occurred at about 246° and another at 380 to 414°, followed by a decrease in rate of weight loss to about 460°, and again by a more rapid loss in weight from 460° to about 490°. A large weight loss occurred at a temperature slightly above 500°.

X-ray diffraction patterns of carbonatated $Ca(OH)_2$ made by water hydration were compared with similar patterns of carbonatated $Ca(OH)_2$ made by vapour-phase hydration. Fig. 3 gives the results for samples conditioned at 25% R.H. followed by carbonatation for 4 h. The CO_2-treated samples were heated in N_2 in the D.T.A. apparatus and rapidly cooled, and an *X*-ray diffraction photograph was taken with the Guinier camera. The '10·4' calcite line and the '10·0' $Ca(OH)_2$ powder line were scanned on a microdensitometer.

Strong calcite lines appeared on *X*-ray diffraction photographs of the unheated water-hydrated material. Corresponding photographs of the vapour-hydrated $Ca(OH)_2$ showed only faint *X*-ray powder lines attributable to calcite. After the vapour-hydrated CO_2-treated material had been heated in a N_2 atmosphere to a temperature of about 330°, however, calcite *X*-ray reflections became quite strong. This indicates that calcium carbonate present as *X*-ray amorphous material crystallised as calcite when the sample was heated to 330°. The $Ca(OH)_2$ lines also showed some sharpening. This temperature of 330° is slightly higher than that of the sharp exothermic peak recorded on D.T.A. diagrams.

The relative intensity of the calcite *X*-ray reflections also confirms the conclusion based on the D.T.A. charts that $Ca(OH)_2$ made by water hydration carbonatated more rapidly than did the vapour-hydrated material. A somewhat similar experiment was performed in which vapour-hydrated $Ca(OH)_2$ carbonatated at 25% R.H. was soaked in water and then dried. The *X*-ray diffraction photograph of this material showed powder lines that could be matched with calcite. The $Ca(OH)_2$ powder lines were also sharpened.

Pre-carbonatated water- and vapour-hydrated $Ca(OH)_2$ was subjected to *X*-ray analysis in a N_2 atmosphere by the

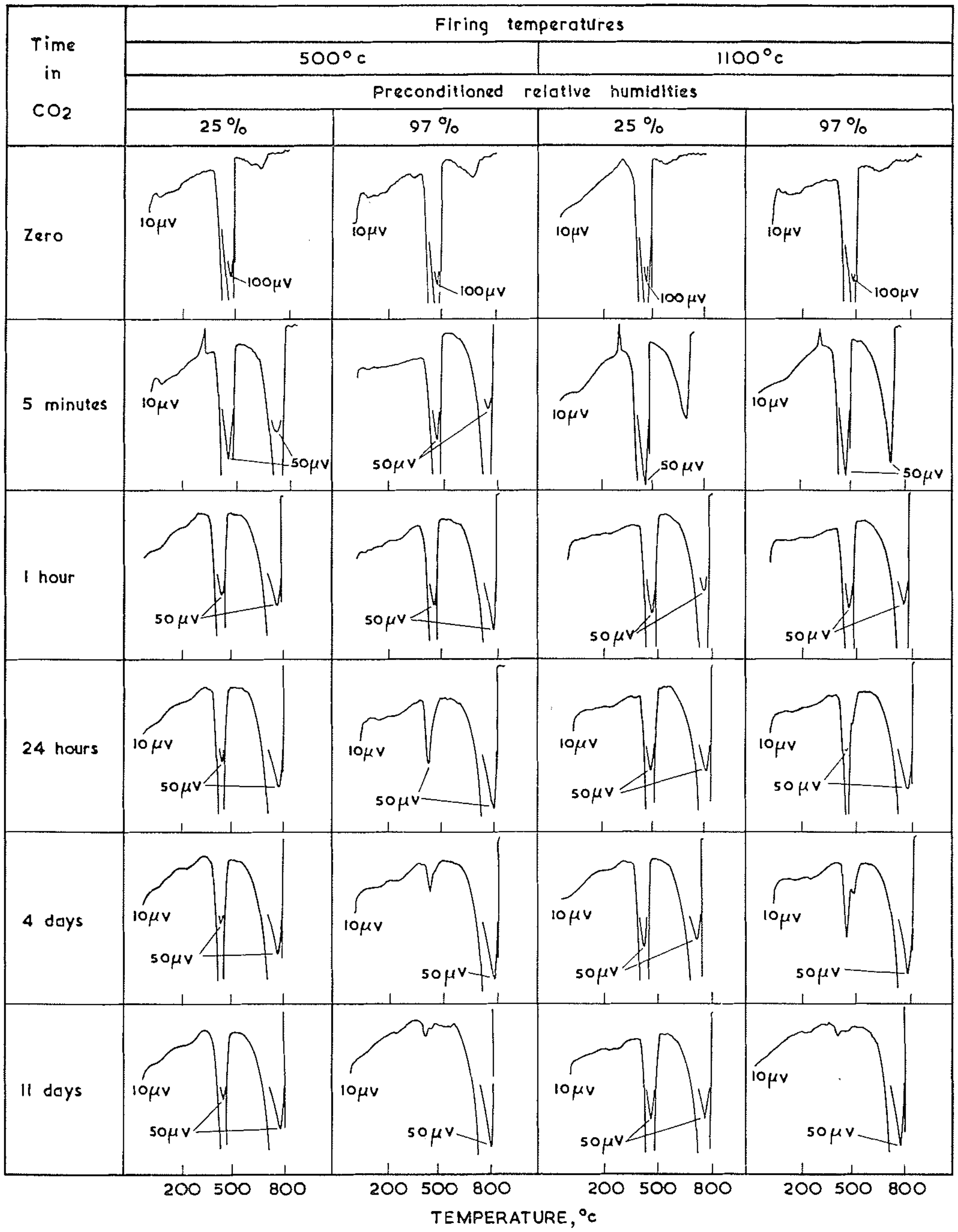

Fig. 2. *Thermograms of water hydrated $Ca(OH)_2$ after increasing times in CO_2*

oscillating heating technique on the diffractometer. An increase in height and sharpness of the '10·4' calcite reflection with increase in temperature was recorded. This reflection continued to increase in intensity in the temperature range from 500° to 700°, following which it rapidly disappeared.

Discussion

Consideration of the sets of D.T.A. curves showed that the rate and course of the carbonatation reaction are affected by the temperature at which the CaO was fired, the method of hydration by which the $Ca(OH)_2$ was prepared, and the relative humidity established prior to carbonatation.

The small endothermic inflection at about 250° on D.T.A. charts was matched on the thermal balance curve by a corresponding weight loss. The temperature is below that at which dehydroxylation takes place and it seems possible that it represents loss of sorbed water held by surface forces.

X-ray diffraction and thermal analysis data indicate that the sharp exothermic peak at about 310° (registered on the D.T.A. charts of the vapour-hydrated $Ca(OH)_2$ carbonatated at 25% R.H. and on the water hydrated $Ca(OH)_2$ carbonatated for less than 1 h) results from crystallisation of calcite from *X*-ray amorphous calcium carbonate and possibly from some crystallisation of $Ca(OH)_2$. There was no signi-

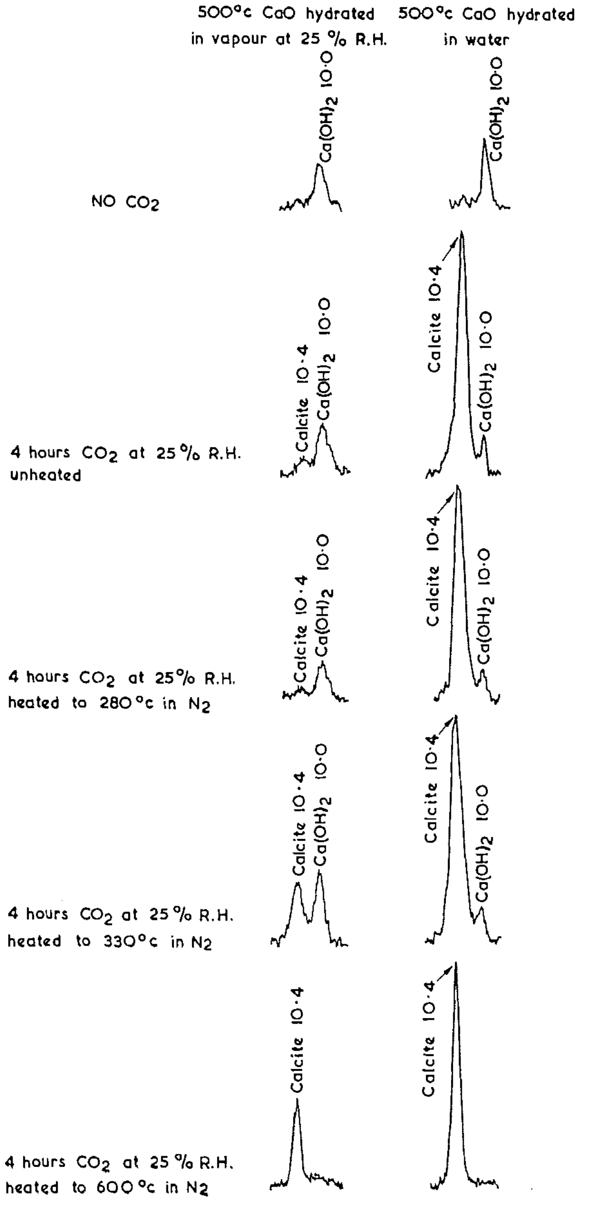

Fig. 3. *Relative height of* 10·0 *$Ca(OH)_2$ vs* 10·4 *Calcite* X*-ray diffraction peak following carbonatation and heat treatment*

ficant weight loss registered at this temperature on curves recorded either by means of the Cahn thermal balance or with a silica spiral. The crystallisation reaction takes place at room temperature in the presence of water, so that the exothermic peak at about 310° was absent on D.T.A. charts of samples pre-conditioned at 97% R.H. It is harder to account for the absence of this peak on thermograms of samples of $Ca(OH)_2$ made by water hydration and pre-conditioned at 25% R.H. prior to CO_2 treatment for periods of time exceeding 1 h. Water is liberated during the carbonatation reaction. A comparison shows that the $Ca(OH)_2$ made by water hydration carbonatated much more rapidly than did the $Ca(OH)_2$ prepared by vapour hydration at either room temperature or 100°. One possibility is that water was liberated sufficiently rapidly during the carbonatation of the water-hydrated samples to raise the relative humidity at the site of the reacting particles to the point at which crystallisation of calcite could occur; in the carbonatation reaction considerable heat is evolved, and some temperature rise may also have occurred. The slower reaction rate of vapour-hydrated $Ca(OH)_2$ may not have liberated water rapidly enough to raise the relative humidity sufficiently for significant crystallisation to take place.

An alternative explanation may also be proposed. The electron micrographs and broadening of the *X*-ray powder lines suggest that the $Ca(OH)_2$ made by vapour-phase hydration is crystallographically less well organised than the $Ca(OH)_2$ formed by water hydration. This diminished crystallographic order in the vapour-hydrated $Ca(OH)_2$ may influence the regularity of the atomic configuration of the $CaCO_3$ that develops on carbonatation if the reaction proceeds via a topotactic mechanism. Hence, relatively much more of the $CaCO_3$ may be *X*-ray amorphous and the presence of the disorganised $Ca(OH)_2$ may more effectively inhibit crystallisation of calcite.

For vapour-hydrated $Ca(OH)_2$ conditioned at 25% R.H., prior to carbonatation and irrespective of the mechanism, the exothermic crystallisation reaction took place only after the temperature had been raised sufficiently to supply the necessary activation energy. The exothermic peak at about 300° is recorded on the thermograms of such samples.

The peak at about 450° on the D.T.A. charts corresponds to breakdown of $Ca(OH)_2$, and the endotherm at about 700° results from breakdown of calcite, as is well known. CaO is the decomposition product in both cases. The relative sizes of these peaks indicate the extent of carbonatation.

The $Ca(OH)_2$ made by water hydration showed a more rapid early rate of carbonatation than did the $Ca(OH)_2$ made by vapour hydration. This effect is most marked in samples conditioned at 25% R.H. The difference in rate is the opposite of that anticipated; the particle size of the $Ca(OH)_2$ made by vapour hydration is known to be less than that of the $Ca(OH)_2$ made by water hydration. The reason for this apparent anomaly is unknown, but it is suggested that it is in some way connected with the amorphous-looking material by which the $Ca(OH)_2$ crystal platelets are enclosed in the samples prepared by vapour-phase hydration. Vapour-hydrated $Ca(OH)_2$ showed a very slow rate of carbonatation with time when conditioned at 25% R.H.

A consideration of peak heights shows that for all samples the rate of carbonatation decreased with time. In the samples pre-conditioned at 97% R.H. there is a tendency for the carbonatation reaction to go to completion more rapidly in the vapour-hydrated $Ca(OH)_2$ than in similarly treated samples of water-hydrated $Ca(OH)_2$. The 450° peak on D.T.A. charts of water-hydrated $Ca(OH)_2$ becomes multiple after an increasing time in CO_2 (Fig. 2). Inversion of aragonite to calcite occurs in approximately that temperature range, but no aragonite lines could be detected on *X*-ray diffraction photographs. It further appears very unlikely that this is the explanation, because the thermal balance curve indicated a multiple weight loss at temperatures approximately the same as those detected by D.T.A. The peak system on the D.T.A. chart shifted to a higher temperature when the analysis was performed in a steam atmosphere, further suggesting that breakdown of $Ca(OH)_2$ is responsible for the peaks. It appears possible that more than one type of $Ca(OH)_2$ was present and that slight structural differences are reflected in differences in the temperature of thermal decomposition. An *X*-ray investigation failed to detect any significant shift in lattice spacings on samples heated to a temperature corresponding to the multiple peak detected on the thermograms.

Consideration of the series of thermograms also showed that the $Ca(OH)_2$ made from CaO prepared by firing at 1100° carbonatated at a slower rate than the corresponding samples of $Ca(OH)_2$ made from CaO fired at 500°.

Decomposition of calcite occurred at a temperature of 800° or less, which is lower than that at which calcite generally decomposes.[10] The doubling of this peak sometimes detected has been attributed to the presence of two types of calcite. The disappearance of the doublet and its replacement by a single peak on a thermogram of a sample stored under vacuum for three days suggests that ageing is a factor that determines whether a peak is double or single.

Conclusions

(1) The $Ca(OH)_2$ made by water hydration is of larger crystallite size than that made by vapour-phase hydration; in the latter, amorphous material appears to be present.

(2) At the same relative humidity, $Ca(OH)_2$ made by vapour hydration carbonatates at a slower rate during early ages than does $Ca(OH)_2$ made by water hydration.

(3) At the same relative humidity there is little difference in response to carbonatation between $Ca(OH)_2$ made by vapour phase hydration at 22° and $Ca(OH)_2$ made by vapour phase hydration at 100°.

(4) Calcite crystallises less readily from carbonatated vapour-phase-hydrated $Ca(OH)_2$ than from $Ca(OH)_2$ made by water hydration in samples pre-conditioned at 25% R.H.

(5) Carbonatation may lead to formation of amorphous calcium carbonate. This crystallises at 310° on heating. If much moisture is present, crystallisation occurs at room temperature.

(6) More than one type of $Ca(OH)_2$ may be present following carbonatation of water-hydrated $Ca(OH)_2$ pre-conditioned at 97% R.H. This decomposes at slightly different temperatures in the 400 to 500° temperature range causing multiple peaks on D.T.A. and thermal balance charts.

(7) The reactivity of the $Ca(OH)_2$ to CO_2 is affected by the firing temperature of the CaO; by the conditions of hydration; and by the relative humidity at the time of carbonatation.

(8) Ageing seems to affect the form of the peak at about 700°.

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[10] See ref. [2], p. 332

EMISSION OF CORROSIVE VOLATILES FROM WOOD

III.* EFFECT OF TREATMENT WITH PROPYLENE OXIDE

By J. D. GRAY, G. C. COCHRANE and P. C. ARNI

A study has been made of the release of corrosive volatiles when wood shavings are sterilised by propylene oxide. Sterilisation of sweet chestnut (*Castanea sativa*), beech (*Fagus sylvatica*), Norway spruce (*Picea abies*), Sitka spruce (*Picea sitchensis*), Douglas fir (*Pseudotsuga taxifolia*) and Scots pine (*Pinus sylvestris*) with propylene oxide at varying relative humidities and subsequent incubation at 48° and 100% R.H. gave a variable release of corrosive volatiles but usually tended to increase the amount of acid released.

Introduction

During the course of a current programme of [illegible] on the emission by wood of corrosive vapours, mainly acetic acid, it was considered of interest to determine whether the release of volatile acid from the wood was exclusively a chemical hydrolysis catalysed by small amounts of acid present in the growing tree or whether the hydrolysis was of microbiological origin. In order to study this aspect of acid release it was necessary to prepare samples of sterilised wood for incubation studies. This was achieved by use of propylene oxide which avoids the use of the high temperature necessary for heat sterilisation.

Samples of freshly felled comminuted sweet chestnut (*Castanea sativa*) and oak (*Quercus robur*) were exposed to vapours of propylene oxide at 21° in a closed container for 48 h. Thereafter, the wood samples were removed and

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