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Ramachandran, V. S.

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DIFFERENTIAL THERMAL METHOD OF ESTIMATING CALCIUM
HYDROXIDE IN CALCIUM SILICATE AND CEMENT PASTES

V.S. Ramachandran
Division of Building Research
National Research Council of Canada
Ottawa, Canada

ANALYZED

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ABSTRACT

DTA is applied to estimate Ca(OH)_2 in cementitious phases by determining the peak areas caused by the decomposition of Ca(OH)_2 to $\text{CaO} + \text{H}_2\text{O}$. In the hydration of C_3S generally, the chemical method yields slightly higher values. DTA is also used as a monitoring technique in preparing a practically Ca(OH)_2 -free product from hydrated portland cement or hydrated C_3S . Hydrated portland cement or C_3S has now been exposed to an unsaturated Ca(OH)_2 solution and extraction continued until the sample indicate no endothermal peak for Ca(OH)_2 . The thermal method permits determination of the rate of formation of Ca(OH)_2 in portland cement hydrated in the presence of 0, 1, 2 and $3\frac{1}{2}$ per cent CaCl_2 .

L'auteur utilise la technique thermique différentielle pour évaluer la teneur en Ca(OH)_2 des phases liantes en déterminant les secteurs pics causés par la décomposition du Ca(OH)_2 en $\text{CaO} + \text{H}_2\text{O}$. Pour l'hydratation du C_3S , la méthode chimique donne généralement des valeurs légèrement plus élevées. La méthode thermique différentielle sert aussi de technique de contrôle dans la préparation d'un produit pratiquement exempt de Ca(OH)_2 à partir de ciment portland ou de C_3S hydraté. L'auteur expose du ciment portland ou du C_3S hydraté à une solution de Ca(OH)_2 non saturée et continue l'extraction jusqu'à ce que l'échantillon ne produise plus de pics endothermiques en présence de Ca(OH)_2 . La méthode thermique permet de déterminer la vitesse de formation du Ca(OH)_2 dans le ciment portland hydraté en présence de 0, 1, 2 et $3\frac{1}{2}$ pour cent de CaCl_2 .

Introduction

A knowledge of the amount of free CH formed during the hydration of C_3S , C_2S and portland cement is essential in following the kinetics and determining the composition of calcium silicate hydrate. Calcium hydroxide, as one of the major phases constituting hydrated cement and hydrated calcium silicates, exerts a significant influence on their physico-mechanical characteristics. In the synthesis of calcium silicate hydrates the determination of $Ca(OH)_2$ permits monitoring of the reactions. Estimation of $Ca(OH)_2$ serves as a method of measuring the reactivity of pozzolanic materials.

Several methods have been suggested for estimating the amount of $Ca(OH)_2$ in cementitious materials. Although calorimetric, X-ray, conductometric titration, and thermal techniques have been used sporadically, the chemical extraction method, involving solvents such as ethylene glycol, acetoacetic acid + isobutyl alcohol (Franke method) and others, seems to be most popular. In the chemical method, however, there is concern that the solvent, in addition to extracting free $Ca(OH)_2$, may attack constituents such as calcium aluminates, high sulfoaluminates, MgO , and the hydrated products of the ferrite phase and calcium silicate hydrate (1-3). It is also recognized that in the chemical method a large number of parameters affect the results and it is somewhat time consuming. As a result, there is a constant search for a reliable alternative method of estimating free $Ca(OH)_2$.

In recent years the thermogravimetric technique (TG) has been suggested for estimating free $Ca(OH)_2$ (4-11). A limitation is that it is not always easy to delineate the temperature intervals corresponding to the weight loss due to $Ca(OH)_2$ decomposition. As well, hydrated products other than $Ca(OH)_2$ may also lose weight in the same temperature range as $Ca(OH)_2$. Although the technique of DTA has been recognized as a valuable tool for the identification of various hydrated and unhydrated phases in cement systems, it has not been applied widely for quantitative purposes (12). A recent paper published by Midgley shows the thermal analysis technique to be very reliable for estimating $Ca(OH)_2$ in set portland cement (13).

In another recent investigation, an estimation of the components in white coat plasters, viz, $CaSO_4 \cdot 2H_2O$, $Mg(OH)_2$, $Ca(OH)_2$, $CaCO_3$ and MgO , was accomplished by applying the differential thermal technique (14). Estimated values corresponded closely to those determined by chemical analysis. It was therefore of interest to extend the method by estimating $Ca(OH)_2$ in other cementitious systems. In the present paper the rate of hydration of C_3S is followed by estimation of $Ca(OH)_2$, using differential thermal and chemical methods of analysis. The differential thermal technique is also applied to investigating the effect of $CaCl_2$ and water/solid ratio on the formation of $Ca(OH)_2$ during hydration of C_3S . Its applicability for monitoring the rate of extraction of $Ca(OH)_2$ from a completely hydrated C_3S and cement using under-saturated $Ca(OH)_2$ solution is also examined.

Experimental

Materials

The sample of tricalcium silicate used in this work was made available by the Portland Cement Association, U.S.A., and had the following composition expressed as a percentage ignited basis:

CaO , 73.88; SiO_2 , 26.17; Al_2O_3 , 0.08; free CaO (ASTM), 0.18; free CaO (Franke), 0.46. Mineralogical analysis: C_3S , 99.33; C_2S , 0.00; C_3A , 0.21; CaO (Franke), 0.46. Fineness: Blaine 3310 cm^2/g .

Calcium hydroxide used for calibration purposes was obtained by calcining Analar Grade CaCO_3 to 1000°C for 3 h and hydrating the resulting CaO in distilled water. The purity of Ca(OH)_2 was checked by TGA and considered satisfactory for drawing the calibration curve.

Portland cement, Type I, of the following compound composition was used for studying the effect of CaCl_2 on its hydration characteristics: C_3S = 51.5 per cent, C_2S = 19.8 per cent, C_3A = 12.8 per cent and C_4AF = 6.6 per cent. The completely hydrated portland cement, Type I, from which the Ca(OH)_2 -free product was prepared had originally the following compound composition: C_3S = 46.5 per cent, C_2S = 24.6 per cent, C_3A = 10.4 per cent and C_4AF = 9.3 per cent.

Calcium chloride hexahydrate of analytical reagent quality was dissolved in water to obtain an approximate concentration of 15 per cent. The exact concentration was determined by the argentometric method and dilutions were made to any required concentration for studying the effect of CaCl_2 on the hydration characteristics of portland cement.

Hydration

The hydration of C_3S was investigated by mixing it with double-distilled water at a water-to-silicate ratio of 0.3. The hydration was carried out in tightly covered polyethylene containers rotated continuously over rollers. At specific intervals of time each sample was dried at 110°C in vacuum for 3 h.

The hydration of portland cement in the presence of CaCl_2 was studied by making cement cubes of 5.1 cm and exposing them at a w/c ratio of 0.25 or 0.4 for 6 h and 12 h, and 1, 2, 3, 7, 14, 28 and 90 days. The concentrations of CaCl_2 in the mixing water were adjusted in such a way that the pastes contained 0, 1, 2 and 3½ per cent CaCl_2 with respect to portland cement.

Extraction of Ca(OH)_2

Discs 0.64 to 0.76 mm thick were cut from cylinders prepared by hydration of C_3S or portland cement at a water/solid ratio 0.5 for about 10 years. They were placed in a cage and exposed to 5 litres of an aqueous solution containing 9.5 mmol/L of CaO . The slicing and extraction were carried out in a CO_2 -free atmosphere.

Analysis

A differential scanning calorimetric (DSC) cell supplied as a module to a Du Pont 990 thermal analysis system was used to obtain thermograms from room temperature to 550°C. In each experiment 20 mg of sample was heated in air at a rate of 10°C/min. For calibration purposes Ca(OH)_2 of known purity was mixed with C_3S in different proportions and endothermal peak areas were plotted against Ca(OH)_2 concentrations. The endothermal peak areas were determined by a planimeter. All samples were dried at 110°C for 3 h in vacuum prior to thermal analysis.

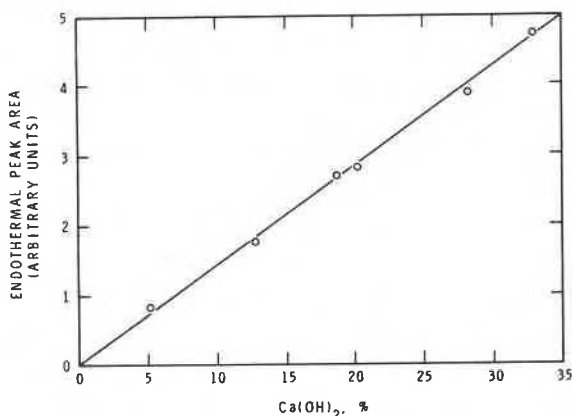


Fig. 1 Calibration curve for estimation of Ca(OH)_2 by differential thermal technique

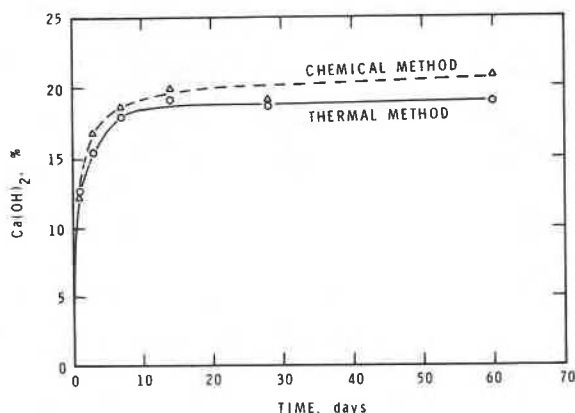


Fig. 2 Amounts of Ca(OH)_2 formed in the hydration of C_3S

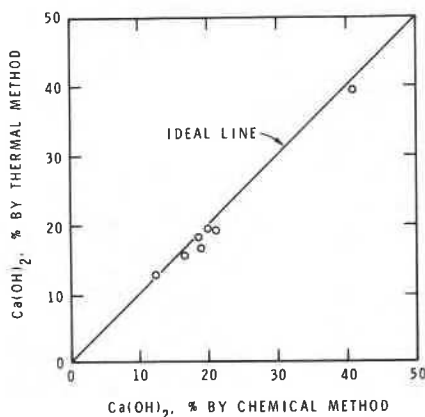


Fig. 3 Comparison of chemical and thermal methods of estimating Ca(OH)_2

The solvent variation method (SVM) was used to estimate Ca(OH)_2 in some samples (1). It consisted of extraction with a mixture of ethyl acetoacetate and isobutyl alcohol in a 3 to 20 ratio by volume. The ratio of the solvent volume to sample weight was varied from 1000 to 3000 mL per gm and the time of each extraction was maintained at 30 min. A plot of the volume of solvent against Ca(OH)_2 extracted gave a straight line whose intercept represented the free Ca(OH)_2 contained in the sample.

Results and Discussion

Figure 1 represents the calibration curve of the endothermal peak areas due to Ca(OH)_2 decomposition in Ca(OH)_2 - C_3S mixtures containing different amounts of Ca(OH)_2 . A good linear relation for samples containing up to about 33 per cent Ca(OH)_2 attests to the applicability of the differential thermal technique for the estimation of Ca(OH)_2 . At a high sensitivity an amount as low as 0.1 per cent Ca(OH)_2 can be estimated.

The relative amounts of Ca(OH)_2 formed at different periods during the hydration of C_3S were estimated by both differential thermal and chemical methods of analysis and the results are compared in Figure 2. Both show that the rate of formation of Ca(OH)_2 is relatively high in the first 7 days, after which it becomes more gradual. Although the general trends are similar, the values resulting from the use of chemical analysis are higher than those from the thermal method. The difference becomes larger as hydration progresses. This, however, can be expected since the chemical method involves attack of the C-S-H phase by the solvent. Figure 3 gives the relation between Ca(OH)_2 values estimated by the differential thermal method and the chemical method; the point at about 40 per

cent Ca(OH)_2 represents a value for an almost completely hydrated C_3S . Although all the points lie close to the ideal line, there is unmistakable evidence that chemical analysis yields slightly higher values.

In the C_3S samples hydrated for different periods the endothermal effect due to decomposition of Ca(OH)_2 (of different crystal sizes) occurs in the temperature range 450 to 550°C. Similar observations have also been made in portland cement pastes. As no other compound in the hydrated cement exhibits thermal effects in the temperature range 450 to 550°C, interference effects are largely avoided.

One method of examining the role of Ca(OH)_2 in hydrated cementitious systems consists of studying the hydrated product from which Ca(OH)_2 is selectively extracted. Any technique adopted to remove free Ca(OH)_2 should not be detrimental to the chemical structure of the hydrates constituting the system. It appears that the least severe treatment, coupled with a good monitoring technique, consists of placing the material in an unsaturated Ca(OH)_2 solution and monitoring from time to time the amount of remaining free Ca(OH)_2 by the differential thermal technique. Differential thermal curves of the sample subjected to extraction for different periods indicate that as the free Ca(OH)_2 is dissolved the intensity of the endothermal peak area due to Ca(OH)_2 decreases gradually (Figure 4). The amount of Ca(OH)_2 remaining at different times is plotted in Figure 5. Almost all Ca(OH)_2 is extracted in about 12 days. Further contact of the material with the extracting solution is not desirable because the possibility exists that lime in the calcium silicate hydrate may be attacked by the unsaturated lime solution. The steep curve at earlier periods in Figure 5 represents a faster rate of extraction of Ca(OH)_2 situated close to the surface of the sample. If a thicker sample had been used, the time interval between extraction of Ca(OH)_2 situated close to the surface and that situated in the interior of the specimen would have been much longer, and the tendency of the extracting solution attacking the C-S-H phase would have increased.

Calcium hydroxide-free portland cement paste was also prepared from a fully hydrated

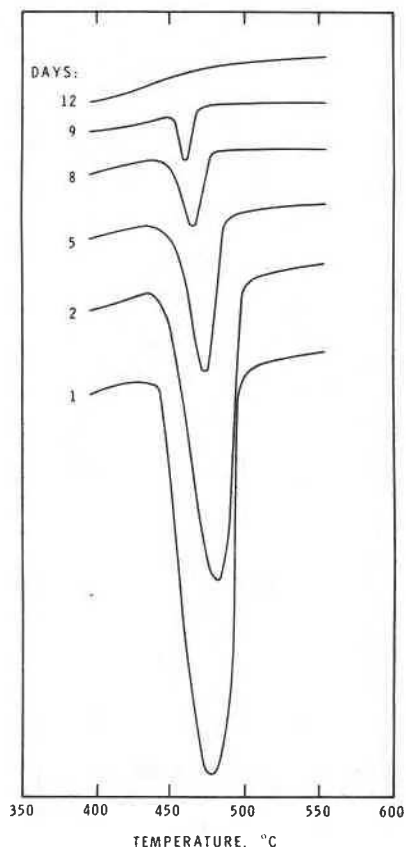


Fig. 4 Endothermal effect due to Ca(OH)_2 in hydrated C_3S exposed to different times of extraction

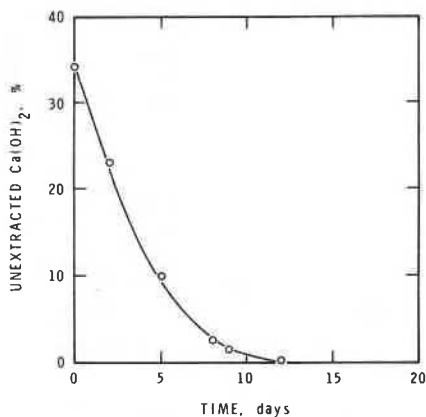


Fig. 5 Influence of time on extraction of Ca(OH)_2 from hydrated C_3S

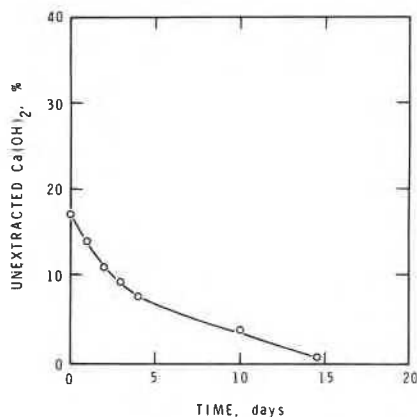


Fig. 6 Influence of time on extraction of Ca(OH)_2 from hydrated cement

cement sample by the technique described above. The results are shown in Figure 6. A fully hydrated portland cement contains less free Ca(OH)_2 than a fully hydrated C_3S paste. It takes somewhat longer, however, to extract all the free Ca(OH)_2 from portland cement paste. It has a higher porosity and lower microhardness than does C_3S paste before extraction, and these factors would be expected to facilitate rather than retard the extraction of Ca(OH)_2 from the cement paste. It is possible that in cement pastes containing aluminate and ferrite phases (in addition to silicate phases) the hydrated lime is enveloped by hydration products much more efficiently than it is in C_3S pastes; thus the permeability of the solid to the extracting solution would be reduced.

One method of following the rate of hydration of cement and Ca-silicates involves determination of free Ca(OH)_2 formed at different times, applying chemical techniques. The applicability of the differential thermal technique of estimating free Ca(OH)_2 produced during the hydration of portland cement containing different percentages of CaCl_2 is illustrated in Figures 7 and 8 (15). In each sample the amount of Ca(OH)_2 formed increases with time, the highest rate occurring in the first 24 h. At a $w/c = 0.25$ all samples show lower amounts of Ca(OH)_2 than do those hydrated at $w/c = 0.4$. This can be explained by the relatively lower degree of hydration in samples made at a $w/c = 0.25$. Rate of hydration, based on amount of Ca(OH)_2 , depends on the total period of hydration and the dosage of the admixture. At 28 days and a $w/c = 0.40$ the rate of hydration in terms of Ca(OH)_2 formation is as follows: cement + 1 to 2 per cent $\text{CaCl}_2 >$ cement + 0 to $3\frac{1}{2}$ per cent CaCl_2 ; at a

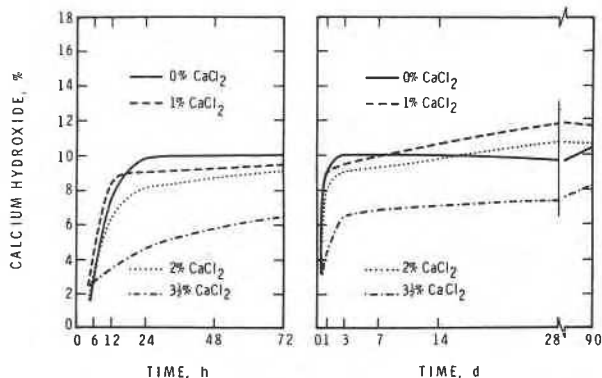


Fig. 7 Influence of calcium chloride on the formation of calcium hydroxide during the hydration of portland cement ($w/c = 0.25$)

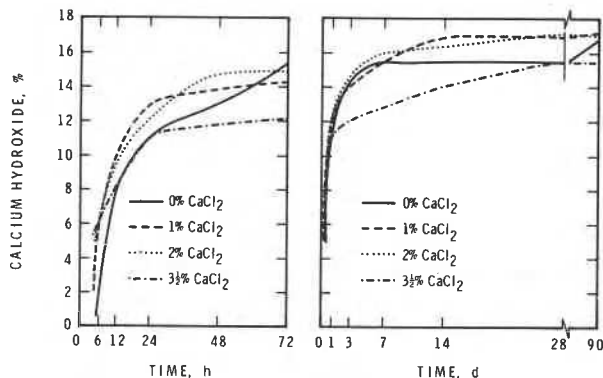


Fig. 8 Influence of calcium chloride on the formation of calcium hydroxide during the hydration of portland cement ($w/c = 0.4$)

DTA, Ca(OH)_2 , CEMENT PASTES, UNDERESTIMATION

w/c = 0.25 the order is: cement + 1 per cent CaCl_2 > cement + 2 per cent CaCl_2 > cement + 0 per cent CaCl_2 > cement + $3\frac{1}{2}$ per cent CaCl_2 . If the rate of hydration is based on the non-evaporable water content, which reflects the total amount of all hydrated products, the rate of hydration is in the order: cement + 2 to $3\frac{1}{2}$ per cent CaCl_2 > cement + 1 per cent CaCl_2 > cement + 0 per cent CaCl_2 (15). This discrepancy has also been observed in the C_3S - CaCl_2 - H_2O system (16). It can be explained by the formation of the C-S-H product with a higher than normal C/S ratio in samples containing $3\frac{1}{2}$ per cent CaCl_2 . Caution should therefore be exercised in using the estimation of Ca(OH)_2 as a basis for comparing the degree of hydration of different materials. The method can be applied to follow the hydration of a particular material per se and to determine the composition of the C-S-H product.

Conclusions

The differential thermal technique appears to be a useful alternative to chemical methods of estimating Ca(OH)_2 in cementitious systems; it is less time consuming, needs only small amounts of sample, and appears to be more reliable. The differential thermal method permits estimation of CaO after conversion to Ca(OH)_2 by autoclaving.

The chemical method overestimates Ca(OH)_2 by including other hydrates in the hydrated cement or calcium silicate; and the X-ray method underestimates Ca(OH)_2 by not registering the presence of microcrystalline or near amorphous Ca(OH)_2 .

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