

HYDRATION OF $\text{Ca}_3\text{SiO}_5\text{-K}_2\text{CO}_3$ SYSTEM*

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ABSTRACT

A thermal analysis study of the effect of various levels of K_2CO_3 upon the hydration reaction of tricalcium orthosilicate, Ca_3SiO_5 or $3\text{CaO}\cdot\text{SiO}_2$, was performed using a Mettler 1 thermoanalyzer. Data obtained by combined differential and gravimetric thermal analyses of nonevaporable water and free-lime contents were used to determine kinetics of Ca_3SiO_5 hydration influenced by the addition of 1 and 5% K_2CO_3 . Attempts were made to study the activation energies of decompositions of hydrates formed by $\text{Ca}_3\text{SiO}_5\text{-H}_2\text{O-CO}_2$ reaction. Calorimetry, scanning electron microscopy, and energy dispersive X-ray analysis were used to support the model derived from thermoanalytical studies.

INTRODUCTION

When tricalcium orthosilicate, Ca_3SiO_5 or $3\text{CaO}\cdot\text{SiO}_2$, one of the major constituents of portland cements, is brought into contact with water, the following hydration reaction starts:



The rate of this reaction and the relative amounts of hydration products formed are known to be dependent on several factors, e.g. temperature of hydration, surface area of the material, presence of admixtures, and the water-to-solid ratio (w/s), i.e., the weight of water used per unit weight of Ca_3SiO_5 . Although $\text{Ca}(\text{OH})_2$ is a crystalline material, the calcium hydrosilicate formed is nearly amorphous; its X-ray powder pattern gives only 1 to 3 characteristic lines. In addition, the composition of the calcium hydrosilicate (usually expressed as CaO/SiO_2 and $\text{H}_2\text{O}/\text{SiO}_2$ ratios) changes during hydration. At the beginning of the hydration reaction, a CaO-rich calcium silicate hydrate is formed, and only small amounts of $\text{Ca}(\text{OH})_2$ are released. After a few hours, hydrates having lower CaO/SiO_2 ratio are formed.

The hydration reaction is exothermic, with heat being released in two steps. Immediately after mixing with water, a sharp heat evolution can be observed, usually

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ascribed to heat of wetting and early topochemical reactions. After 5–15 min, the reaction slows down, followed by an induction period with negligible rate of heat evolution observed. Depending upon the conditions of hydration, the induction period may last from an hour to a few days. It is generally accepted that, in this period, the liquid phase of the system becomes supersaturated with respect to $\text{Ca}(\text{OH})_2$. When the first crystal nuclei of $\text{Ca}(\text{OH})_2$ are formed, the $\text{Ca}_3\text{SiO}_5\text{-H}_2\text{O}$ reaction again accelerates. After reaching a maximum, the reaction (and the heat evolution) decelerates and, after approximately 24 hours, the reaction proceeds very slowly to final hydration. The ultimate degree of hydration achievable depends upon the original w/s ratio, because the newly formed hydration products, deposited in the water-filled pores between the Ca_3SiO_5 particles, have a larger specific volume than the anhydrous Ca_3SiO_5 . Therefore, at low w/s ratio, where the porosity is small, 100% hydration cannot be reached.

To increase the rate of Ca_3SiO_5 reaction with water, various admixtures can be used, with the most common being CaCl_2 . Although the exact mechanism of $\text{CaCl}_2\text{-Ca}_3\text{SiO}_5\text{-H}_2\text{O}$ interaction is not known in detail, the change in the Ca^{2+} concentration of the liquid phase plays an important role. Other known accelerators of cement hydration are alkali carbonates. Most of the available data on alkali carbonates were obtained for cement and not for pure cement minerals, such as Ca_3SiO_5 ¹⁻³. Comparatively little information is available on the $\text{Ca}_3\text{SiO}_5\text{-Na}(\text{K})_2\text{CO}_3$ interaction^{4,5}. In these studies, only the effects caused by the presence of alkali carbonates have been described. Very little is known of the mechanisms of these reactions. Stein reported that Na_2CO_3 accelerates the hydration of Ca_3SiO_5 in cement, but retards the conversion of the high sulfate calcium aluminate hydrate, $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot 32\text{H}_2\text{O}$, into its low sulfate form, $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaSO}_4\cdot 12\text{H}_2\text{O}$, through the formation of calcium carboaluminate, $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCO}_3\cdot 11\text{H}_2\text{O}$ ¹. Niël described the effects of K_2CO_3 upon setting and hardening of cement mortars². Using X-ray, infrared and chemical analyses, Niël related changes in these parameters to the concentrations of K_2CO_3 used. Brunauer and coworkers studied the cement- K_2CO_3 interaction for low w/s cement pastes in the presence of Ca-lignosulfonate³ and suggested possible mechanisms for the reactivity of K_2CO_3 in this complicated system. They did not attempt to clarify the K_2CO_3 reactivity with pure cement minerals. Mori *et al.*⁴ and Skalny *et al.*⁵ described complicated heat effects produced by additions of alkali carbonates to the $\text{Ca}_3\text{SiO}_5\text{-H}_2\text{O}$ system. Mori *et al.*, in addition, described some differences in the morphology of calcium silicate hydrates formed in the presence and in the absence of alkali carbonates.

The objective of the present study, therefore, has been to clarify the effect of K_2CO_3 upon the hydration of Ca_3SiO_5 and to define the functions of K^+ and CO_3^{2-} ions in the $\text{Ca}_3\text{SiO}_5\text{-K}_2\text{CO}_3\text{-H}_2\text{O}$ system.

EXPERIMENTAL PROCEDURES

Tricalcium silicate having a surface area of ca. $3500\text{ cm}^2\text{ g}^{-1}$ (measured by Blaine method) was used in the study. The free $\text{Ca}(\text{OH})_2$ content of this material was

0.06%. Samples were prepared by mixing Ca_3SiO_5 with 0.5 part by weight of distilled water containing 0, 1 and 5% of K_2CO_3 . Samples were cured for various time periods in a 100% relative humidity chamber at a temperature of 35°C . Precautions were taken to prevent carbonation of the samples by atmospheric CO_2 .

Hydration was stopped, and samples were dried in vacuum desiccators for at least two weeks at pressures corresponding to the vapor pressure of H_2O at a dry-ice/methanol temperature of 78°C^- .

DTA/TGA patterns were obtained for dried samples using a Mettler Thermo Analyzer 1. The tests were conducted on 10-mg samples at a $10^\circ\text{C min}^{-1}$ heating rate in flowing nitrogen (5 l h^{-1}) at sensitivities of 0.1 mg in^{-1} and $5 \mu\text{V in}^{-1}$ ($\sim \frac{1}{2}^\circ\text{C}$) for the TGA and DTA, respectively. Selected samples were analysed simultaneously by a Balzers Quadrupol Mass Spectrometer QMG 101 attached to the Mettler Thermo-analyzer.

For the kinetics of decomposition studies, 300-mg samples were used at sensitivities of 1 mg in^{-1} (TGA) and $10 \mu\text{V in}^{-1}$ (DTA). The heating rates were 6, 10, 15 and $25^\circ\text{C min}^{-1}$.

The hydration reactions of Ca_3SiO_5 in the presence of various amounts of K_2CO_3 were studied using a semi-adiabatic calorimeter. Each reaction cell was filled with 2 g of Ca_3SiO_5 , sealed, and placed into a water-bath for equilibration. After stabilization at the bath temperature, water of the same temperature (25°C), containing various amounts of K_2CO_3 , was injected into each sample cell by hypodermic syringe through a rubber cup. Subsequently, mixing was accomplished by vibrating each reaction cell for 10 sec. Instantaneous readings were made on a multipoint chart recorder.

Morphology of the hydration products was investigated with a JSM-U3 Scanning Electron Microscope (SEM), with energy dispersive X-ray analysis (EDAX) used for elemental analysis.

The non-evaporable water content, w_n , was determined from the ignition loss at 1000°C of the dried samples. Degree of hydration, $X = w_n/w_n^*$, was determined assuming that the combined water needed for complete hydration of Ca_3SiO_5 is 23%. All data were calculated in g/g of original material.

The free $\text{Ca}(\text{OH})_2$ was determined from the DTA/TGA patterns; corrections were made for carbonation caused by atmospheric CO_2 and the presence of K_2CO_3 . It was assumed that all CO_2 is present in form of CaCO_3 . This assumption may not be absolutely correct as shown by recent experiments performed by the authors⁶.

RESULTS AND DISCUSSION

A typical thermogram of a hydrated tricalcium silicate is shown in Fig. 1. In nitrogen atmosphere, dried samples begin to decompose well below 100°C . It is generally believed that the endotherm (or overlapping endotherms) and the large weight loss in the region $100\text{--}300^\circ\text{C}$ is caused by the decomposition of nearly amorphous calcium silicate hydrates. Figure 1 indicates that, in this case, at least two (but

possibly more) hydrates are decomposed simultaneously. At the same temperature at which peak A' is reached, the slope of the TGA curve changes substantially at point A on the TG curve.

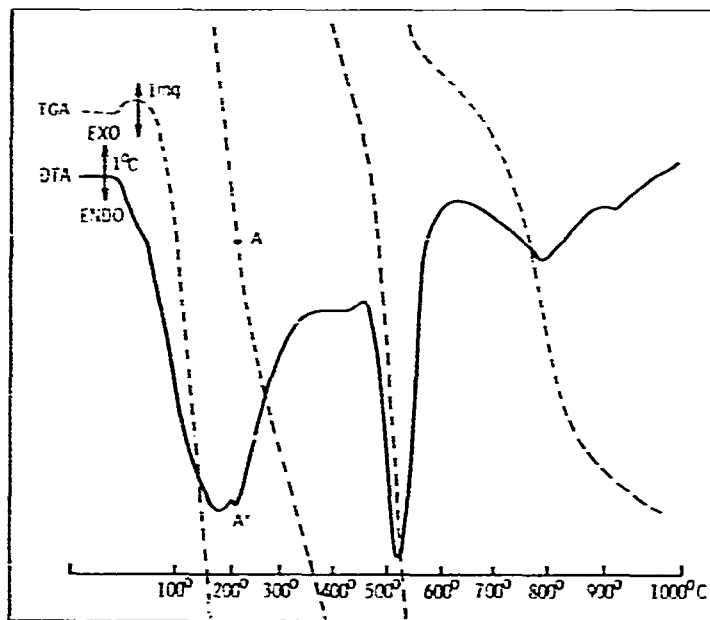


Fig. 1. Thermogram of hydrated tricalcium silicate at a heating rate of 15 C min^{-1} in a flowing nitrogen atmosphere (5 l h^{-1}). Point A indicates a change in rate of weight loss corresponding to the endotherm A'.

The small endotherm at about 450°C and the endotherm and weight loss at about 500°C represent the decomposition of $\text{Ca}(\text{OH})_2$. It is accepted that the DTA endotherm and weight loss at around 800°C is caused by the decomposition of calcium carbonate. The small endotherm above 900°C represents a Ca_3SiO_5 phase transformation. It is our belief that this is an oversimplified description. There is some evidence that a considerable amount of CO_2 is evolved at much lower temperatures than generally accepted⁶. Therefore, it is believed, the results given in Table I may not be quantitatively correct; however, they can be compared with each other and with other data given in the literature.

It has been found that the $\text{Ca}_3\text{SiO}_5\text{-H}_2\text{O}$ system hydrates at a much faster rate of reaction in the presence of K_2CO_3 . The degree of hydration, a function of the non-evaporable water content, is proportional to the K_2CO_3 concentration. As mentioned earlier, the composition of the hydration products changes with the time of hydration. This can be seen in the last column of Table I, which shows the CaO/SiO_2 ratio of the calcium silicate hydrate formed. In all shown cases, this ratio decreases with progressing hydration. With increasing amounts of K_2CO_3 , the CaO/SiO_2 ratios decrease for the same times of hydration. However, when compared on the basis of degree of hydration, they seem to be consistent. For example, the 0% K_2CO_3 sample at 24 h

TABLE I
HYDRATION OF Ca_3SiO_5 IN THE PRESENCE OF K_2CO_3

Time of hydration (h)	K_2CO_3 (%)	Nonevaporable water ($\text{gH}_2\text{O/gC}_3\text{SiO}_5$)	Degree of hydration (%)	CaO/SiO_2 ratio of C-S-H (mol mol)
0.5	0	0.0028	1.2	2.52
1	0	0.0048	2.1	2.49
6	0	0.0255	11.1	2.39
24	0	0.0825	35.8	2.17
336	0	0.1334	58.0	1.97
0.5	1	0.0147	6.4	2.49
1	1	0.0260	11.3	2.39
6	1	0.0825	35.9	2.19
24	1	0.1012	44.0	2.13
336	1	0.1374	59.7	1.98
0.5	5	0.0569	24.7	2.36
1	5	0.0755	32.8	2.24
6	5	0.1075	46.7	2.15
24	5	0.1185	51.5	2.04
336	5	0.1360	59.1	1.89

of hydration and 1% K_2CO_3 sample at 6 h of hydration have an equal nonevaporable water content and, at the same time, the same CaO/SiO_2 ratio. This implies that the presence of K_2CO_3 increased the rate of reaction but did not influence the composition of the calcium silicate hydrate.

Figure 2 shows the change of hydration rate caused by the presence of K_2CO_3 . The ratio $\Delta w_n/\Delta t$ represents the change in the nonevaporable water content with time. The largest differences are in the early periods of reaction, while later, when ca. 40% of the Ca_3SiO_5 is hydrated, the differences in reaction rate are negligible. This shows very clearly that K_2CO_3 influences the process of formation of hydrates at the onset of hydration. This activity is, possibly, a result of changes in the composition of the liquid phase which, in turn, may influence the formation of calcium silicate hydrate crystal nuclei. This is in agreement with Mori *et al.*⁴, who found that, in the presence of Na_2CO_3 , tricalcium silicate dissolved more vigorously than in its absence. The Ca(OH)_2 formed reacted immediately with CO_3^{2-} to form CaCO_3 , and some of the evolved CaO formed calcium silicate hydrate.

Complicated heat evolution effects caused by the presence of K_2CO_3 in the hydration of tricalcium silicate are shown in Fig. 3. In the absence of K_2CO_3 and upon mixing with water, a sharp heat evolution peak is observed and is believed to be due to the heat of wetting and the heat of topochemical reactions. For pure tricalcium silicate, the rate of heat evolution decreases after a few minutes, followed by a period of ca. 3 h with no measurable heat evolution, then accelerates to a maximum at ca. 10 hours and, subsequently, decelerates. In the presence of K_2CO_3 , the heat evolution pattern is more complicated. In addition to the initial peak, the sample containing 1% K_2CO_3 exhibited three more peaks at approximately 10 min and 2 and 6½ hours.

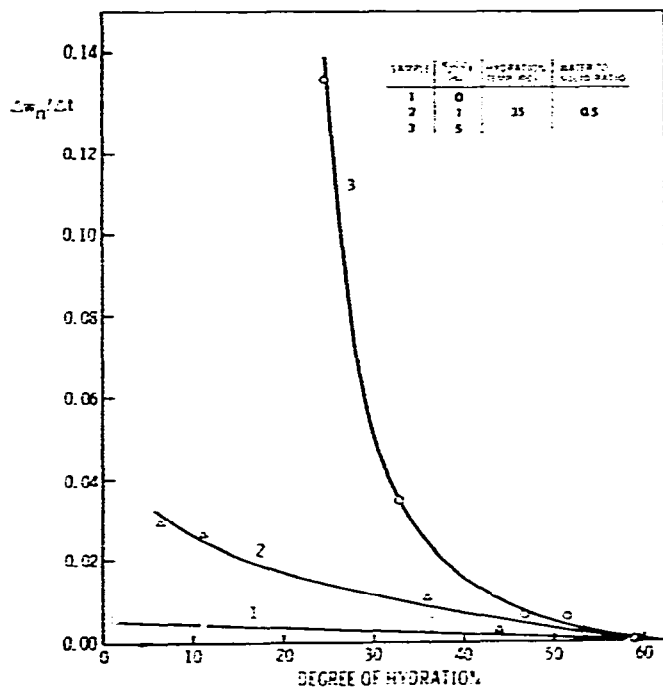


Fig. 2. Influence of K_2CO_3 content upon the rate of early reaction in the $Ca_3SiO_5-H_2O$ system at $35^\circ C$.

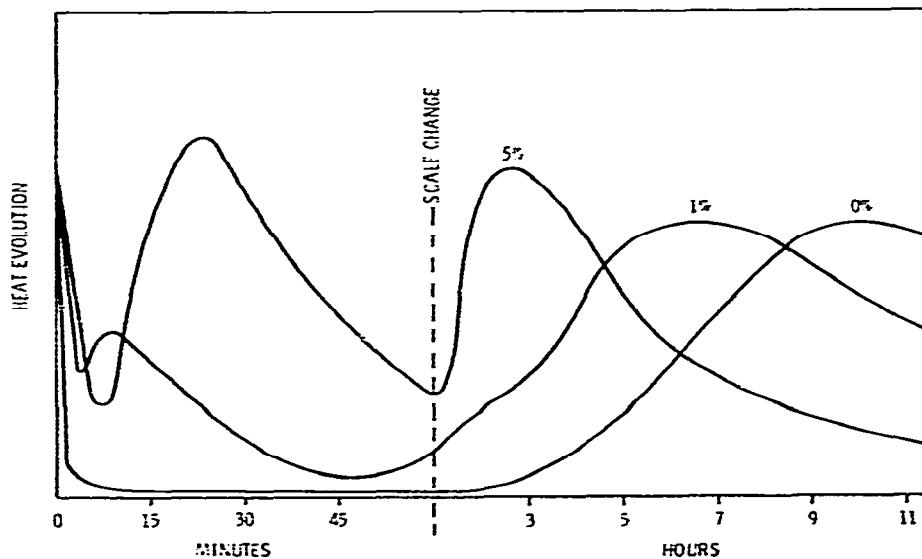


Fig. 3. Heat evolution (arbitrary units) curves as a function of time for pure tricalcium silicate and with 1 and 5% additions of K_2CO_3 being hydrated at a w/s ratio of 0.5, at $25^\circ C$.

The sample containing 5% K_2CO_3 exhibited only two additional peaks; however, the second peak may have been missed, or it may overlap the first peak. The last peak represents the post-induction period of Ca_3SiO_5 hydration. As can be seen, this hydration is accelerated—the respective peaks for 0, 1 and 5% K_2CO_3 -containing

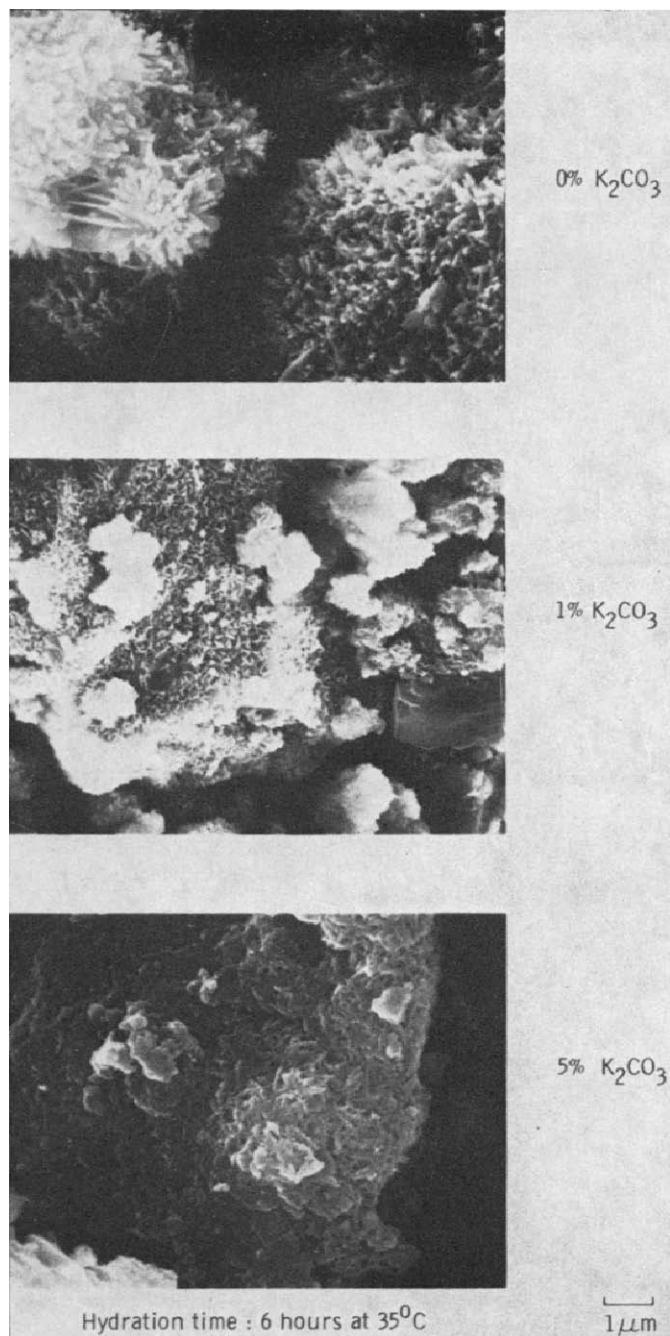


Fig. 4. Changes in the morphology of the Ca_3SiO_5 hydration products due to the presence of K_2CO_3 . Hydration time: 6 h at 35°C.

samples are reached after 10, 6½ and 3 hours. The physical meaning of the other two peaks is not clear. The subsequent accelerations and decelerations of reaction are most probably caused by several simultaneously proceeding processes, such as formation of first hydrosilicates on the surface of unhydrated particles, precipitation of CaCO_3 , diffusion through the layer of hydrates, formation of nuclei of calcium silicate hydrates and $\text{Ca}(\text{OH})_2$, etc. It is possible that the increase in the rate of reaction in the post-induction period of samples containing K_2CO_3 is caused by the presence of calcium silicate hydrate nuclei formed in the first min of hydration.

The SEM-EDAX study established the morphology of hydration products and determined the location of potassium in the hydrates. Typical morphologies obtained in samples hydrated with different amounts of K_2CO_3 are shown in Fig. 4. In the absence of K_2CO_3 , after 6 h of hydration, only normal aciculae of outermost calcium silicate hydrate were observed. In agreement with the calculations of free $\text{Ca}(\text{OH})_2$ from the thermal analysis data, only very small amounts of calcium hydroxide were observed. Later, the $\text{Ca}(\text{OH})_2$ content increased, while the morphology of calcium silicate hydrates remained unchanged, and the density of the samples increased substantially.

In the presence of 1% K_2CO_3 , calcium hydroxide crystals were found after 1 h of hydration. The morphology of the calcium silicate hydrates changed slightly, resembling the "honeycomb" morphology of Ca_3SiO_5 pastes hydrated in the presence of CaCl_2 (e.g. refs. 7, 8, 9).

In the presence of 5% K_2CO_3 large amounts of platy $\text{Ca}(\text{OH})_2$ were formed. The calcium silicate hydrate lost its distinct needle-like morphology, as can be seen in the bottom picture of Fig. 4.

Figure 5 shows, at low magnification, a Ca_3SiO_5 sample hydrated at 35°C for 6 hours in the presence of 5% K_2CO_3 . At marked locations, X-ray measurements were taken by EDAX. Visible amounts of K are located in the calcium silicate hydrate only. The large crystals of $\text{Ca}(\text{OH})_2$ contain small amounts of Si, probably in the form of entrapped particles of calcium silicate hydrate. It is not clear if potassium-containing calcium silicate hydrates are formed, as suggested by Sudoh and Mori¹⁰, or if a potassium containing compound is intermixed with the silicate hydrates.

An attempt to quantify the kinetics of decomposition of the $\text{Ca}(\text{OH})_2$, CaCO_3 and calcium silicate hydrate formed during the hydration reactions of pure tricalcium silicate was made using the Kissinger analytical technique¹¹. For this analysis, thermograms were obtained for heating rates of 6, 10, 15 and 25°C min⁻¹. The resulting Arrhenius plot for $\text{Ca}(\text{OH})_2$ is shown in Fig. 6. The calculated activation energy of 42.0 kcal mole⁻¹ from these data is in good agreement with the literature values for pure $\text{Ca}(\text{OH})_2$ (35–45 kcal mole⁻¹) published by Dave and Chopra¹². One contradictory literature value is that of Mikhail *et al.*,¹³ who obtained 14.3 kcal mole⁻¹ for the isothermal decompositions of $\text{Ca}(\text{OH})_2$ formed in the hydration of β -dicalcium silicate. Recent studies by Maycock *et al.*⁶ have shown that, at the same time and temperature required for the decomposition of $\text{Ca}(\text{OH})_2$ and liberation of H_2O , there is a simultaneous evolution of a considerable amount of CO_2 from some undefined

source. This contribution to the isothermal weight loss data undoubtedly will lead to erroneous values for the kinetics of the decomposition of $\text{Ca}(\text{OH})_2$. Thus, of the published values for the decomposition of $\text{Ca}(\text{OH})_2$, those of Mikhail et al.¹³ may be unreliable due to undetected presence of CO_2 .

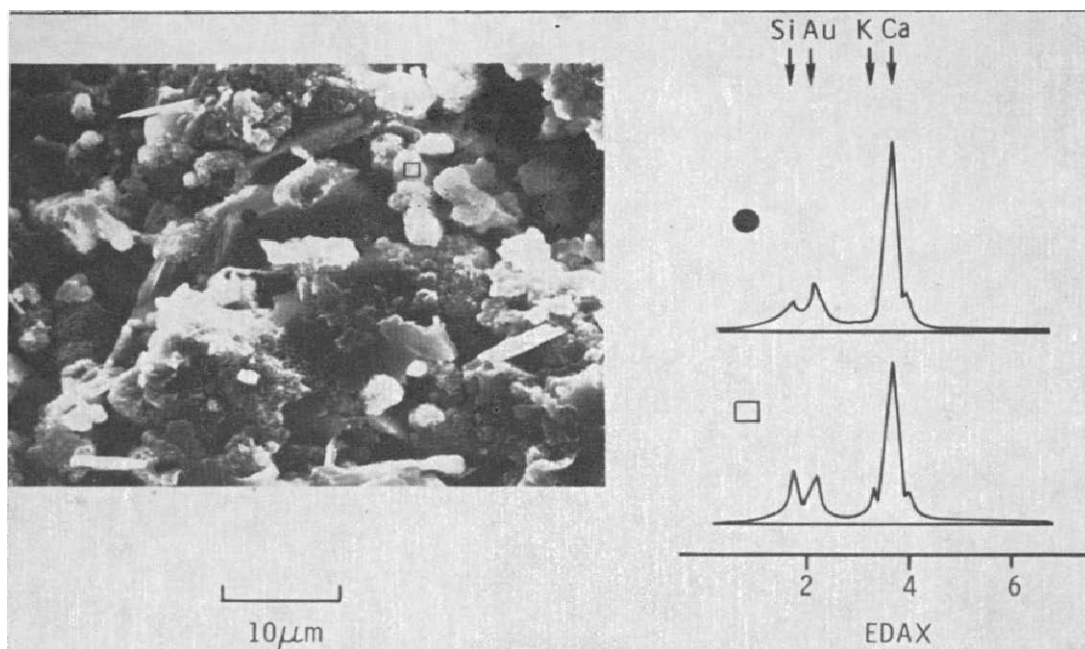


Fig. 5. Scanning electron micrograph and EDAX spectra of $\text{Ca}_3\text{SiO}_5 + 5\% \text{K}_2\text{CO}_3$ hydrated at 35°C for 6 hours.

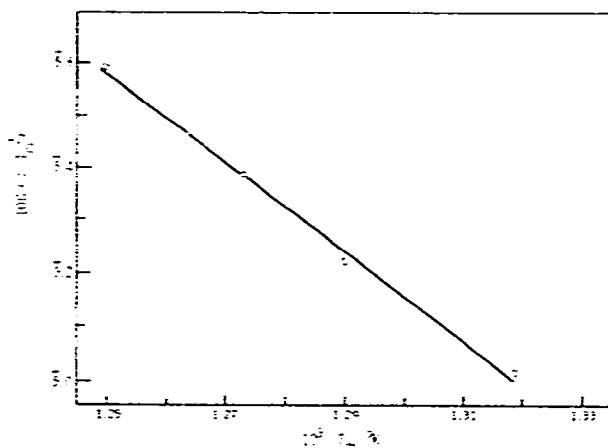


Fig. 6. Kissinger kinetic analysis of the thermal decomposition of the Ca_3SiO_5 hydration product $\text{Ca}(\text{OH})_2$. The temperature T_m is the temperature of the peak of the decomposition endotherm which is a function of the heating rate ϕ .

The activation energies obtained for the decomposition of calcium silicate hydrate and CaCO_3 were 11 and 38 kcal mole⁻¹, respectively. The latter result is in good agreement with literature data of approximately 40 kcal mole⁻¹ (refs. 14, 15). No kinetic data were found in the literature on the decomposition of nearly amorphous calcium silicate hydrate.

Tenoutasse reported for the activation energy of Ca_3SiO_5 hydration a value of 9.8 kcal mole⁻¹ (ref. 16). The activation energies were the same, within experimental error, for both pure and K_2CO_3 -doped Ca_3SiO_5 hydrates.

CONCLUSIONS

Results of the present investigation can be summarized as follows:

(1) K_2CO_3 produces multiple heat effects in the early hydration of Ca_3SiO_5 . Both calorimetric and DTA/TGA studies have shown that its presence accelerates the rate of Ca_3SiO_5 hydration.

(2) Energy dispersive X-ray analysis has shown that the near-amorphous calcium silicate hydrate acts as a sink for the K^+ ions. The exact chemical and/or physical nature of its presence in the hydrate is unknown.

(3) CO_3^{2-} is incorporated in the hydrated paste as CaCO_3 as well as in other forms; a substantial amount forms a part of calcium silicate hydrate and is evolved at much lower than expected temperatures.

(4) It is possible, when proper combinations of experimental techniques are used, to perform a kinetic analysis of such complicated systems as Ca_3SiO_5 - K_2CO_3 - H_2O .

(5) It is likely that both K^+ and CO_3^{2-} play an important role in the acceleration of hydration of Ca_3SiO_5 . Studies addressing the role and location of these ions in hydrates, particularly that of CO_3^{2-} , are continuing and will be published in the future.

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