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Hydration of tricalcium germanate

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The hydration characteristics of tricalcium germanate were examined. Kinetics of tricalcium germanate hydration, and hydration product morphologies and compositions were determined at 5 °C intervals between 5 and 70 °C. Complete hydration was rapidly achieved. X-ray diffraction indicated that tricalcium germanate reacted completely within 2 h at all the temperatures investigated. However, a constant value for an Arrhenius activation energy could not be determined. At hydration temperatures above 45 °C a small heat peak, which preceded the main calorimetric peak, appeared in the calorimetric curves. Calcium hydroxide was rarely observed by SEM for hydration at temperatures below 45 °C. Dense regions of calcium hydroxide were readily observed for hydration above this temperature. In contrast to the hydration of tricalcium silicate, an induction period was not observed nor was an extended period of diffusionally controlled reaction. Calcium germanate hydrate was fibrous with the fibre thickness exhibiting a temperature dependence. Hydration product compositions were determined by thermal gravimetry. Expressing the composition of calcium germanate hydrate as $(CaO)_{3-x}\,GeO_2 \cdot nH_2O$, the value of $3-x$ decreases from 1.68 to 1.59 with increasing temperature from 5–70 °C. The values obtained for n varied inconsistently between 2.4 and 3.3. The unit cell of the calcium germanate hydrate was determined to be monoclinic. Cell parameters were $a = 1.851$, $b = 1.147$, $c = 0.531$ nm and $\beta = 98.10°$.

1. Introduction

In analogy with tricalcium silicate and tricalcium aluminate, tricalcium germanate is a basic oxide which undergoes low-temperature hydration reactions in a similar fashion to these cementing compounds. Although very few studies have been carried out, the hydration reactions of the calcium germanates have been reported to proceed more rapidly and achieve completion more readily than those of the related silicate compounds [1, 2]. Sample and Brown [3] studied the hydration characteristics of tricalcium silicate–tricalcium germanate solid solutions and observed the overall reactivity to increase significantly with increasing proportion of GeO_2. Depending on particle size, the hydration of pure tricalcium germanate reaches completion within a few hours [1, 3]. Toropov and Shirvinskaya [1] credit this difference in kinetics to the ionic sizes of germanium and silicon. The germanium ion is larger than the silicon ion and forms weaker bonds with oxygen.

Depending on the conditions of reaction, a variety of calcium germanate hydrates have been reported. Wieker *et al.* [4] reported the formation of $3CaO \cdot 3GeO_2 \cdot H_2O$ by reaction of equimolar mixtures of CaO and GeO_2 over the temperature range 100 to ~ 450 °C. Evdokimov and Sokolova [5] prepared $2CaO \cdot GeO_2$, $CaO \cdot GeO_2$, and $CaO \cdot 2GeO_2$ by reaction of CaO with $GeCl_4$ and reported these compounds to hydrate to $CaO \cdot GeO_2 \cdot H_2O$ at 420 °C and to $2CaO \cdot GeO_2 \cdot H_2O$ at low temperature. Ryskin *et al.* [6] prepared α-$CaO \cdot GeO_2 \cdot H_2O$ at 140 °C and characterized the material by X-ray diffraction and infrared spectroscopy. Zagorodnyuk *et al.* [7] prepared $5CaO \cdot 5GeO_2 \cdot H_2O$ by precipitation from solutions of $Ca(NO_3)_2$ and GeO_2 followed by heating to 100 °C. Guyader and Lang [8] formed $5CaO \cdot 2GeO_2 \cdot xH_2O$ by the room-temperature hydrolysis of the nitrides while Toropov and Shirvinskaya [1] reported the formation of $CaO \cdot GeO_2 \cdot nH_2O$ and $1.5CaO \cdot GeO_2 \cdot nH_2O$ at room temperature. The latter calcium to germanium ratio is comparable to the calcium to silicon ratio in calcium silicate hydrate, $1.7CaO \cdot SiO_2 \cdot nH_2O$. Of these studies, only that of Evdokimov and Sokolova [5] involved the formation of calcium germanate hydrates by hydration of a calcium germanate.

Because of its chemical similarity to tricalcium silicate and the limited work carried out on tricalcium germanate, its hydration was investigated at temperatures from 5–70 °C. The reactivity of tricalcium germanate allows it to hydrate completely and it may provide a suitable model to allow further understanding of the kinetics of tricalcium silicate hydration. Therefore, the kinetics of tricalcium germanate hydration was investigated. In addition, the compositions of the hydration products were determined and their morphologies examined. Finally, the unit-cell dimensions of calcium germanate hydrate were determined.

2. Experimental procedure

Tricalcium germanate, $3CaO \cdot GeO_2$, was synthesized by reacting $CaCO_3$ and GeO_2 at a molar ratio of 3 : 1

at 1500 °C. The precursors were placed in ethanol and pulverized in a vibratory mill for 36 h to ensure homogeneity. The ethanol was evaporated at 55 °C. The fine powder was calcined at 1000 °C for 0.5 h then fired at 1500 °C for 6.5 h. The resulting $3CaO \cdot GeO_2$ was ground by mortar and pestle and then milled to a median particle size of 1.5 μm. X-ray diffraction indicated the $3CaO \cdot GeO_2$ obtained was phase pure.

Heat evolved during the hydration of $3CaO \cdot GeO_2$ was measured by isothermal calorimetry. In the calorimetric method used, $3CaO \cdot GeO_2$ was placed in a gold-plated copper cup. The cup was completely surrounded by thermopiles which produce an e.m.f. output proportional to their exposure to temperature gradients. A constant temperature was maintained by water circulation from a constant-temperature bath. The $3CaO \cdot GeO_2$ and water were separately equilibrated and the water was injected into the powder through a syringe to initiate reaction. $3CaO \cdot GeO_2$ was hydrated at a water to solids ratio of unity at constant temperatures ranging from 5–70 °C in 5 °C intervals. At higher temperatures, the sample cup was wrapped with microwaveable plastic to minimize the possible evaporation of water. The voltage output from the calorimeter was digitized by a computer system. A 3 s averaged e.m.f. was read every 6 s, scaled by a constant factor to milliWatts and stored. Further data processing yielded the heats of reaction by using the trapezoid rule to integrate the heat evolution data. Because complete hydration was achieved, the fractions of tricalcium germanate reacted at each temperature were obtained from the normalized ΔH_r–time curves, assuming a linear relationship exists. Complete hydration was verified by removing the specimens from the calorimeter, quenching them in acetone to stop any further reaction, and carrying out X-ray diffraction analyses.

Tricalcium germanate was also hydrated at a liquid to solids ratio of 30 at 25 and 70 °C. Variations in solution pH were measured with an Orion 920 pH meter that utilized an automatic temperature-compensating probe.

The hydration products formed at different temperatures were characterized by thermal gravimetry and X-ray diffraction analyses. The changes in weight with heating were used to determine the number of waters of hydration, n, in the calcium germanate hydrate, the moles of $Ca(OH)_2$ formed, x, and the mole ratios in the hydration reaction

$$3CaO \cdot GeO_2 + (x + n)H_2O \rightarrow (3 - x)CaO \cdot GeO_2 \cdot nH_2O + xCa(OH)_2 \qquad (1)$$

The unit cell of $(3 - x)CaO \cdot GeO_2 \cdot nH_2O$ was calculated from powder X-ray diffraction data obtained from a sample of tricalcium germanate hydrated at 45 °C. Five computational methods were applied with complete agreement on unit-cell dimensions [9–13].

SEM was used to observe the morphological variations in the calcium germanate hydrates formed and EDX analysis was used to determine the presence of calcium and germanium in the phases observed.

3. Results and discussion

3.1. Kinetics of hydration

The tricalcium germanate used in this study was found to react completely within 2 h when hydrated at constant temperatures between 5 and 70 °C. Complete hydration was established by X-ray diffraction analyses of the specimens immediately after their removal from the calorimeter. The curves showing the rates of heat liberation ($W\,mol^{-1}$ tricalcium germanate) are presented in Fig. 1. For ease of representation, the calorimetric curves are grouped into three temperature ranges. For reaction at temperatures between 5 and 25 °C, the heat evolution characteristics are well behaved. In general, the higher the temperature the more rapid is the hydration process. The magnitudes of the calorimetric curves increase with increasing temperature and the peaks in these curves occur at shorter times as the reaction temperature increases. However, there is a negligible difference in hydration kinetics between 20 and 25 °C. At hydration temperatures between 25 and 45 °C, the calorimetric peaks broaden with increasing temperature and there is a trend for the maxima in the peaks to occur at longer times. As observed for the calorimetric curves obtained at 20 and 25 °C, the curves at 40 and 45 °C are not greatly different. At hydration temperatures above 45 °C, the trend in heat evolution is again reversed and the calorimetric peaks sharpen with maxima occurring at shorter times. Associated with this behaviour is the appearance of second peaks in the calorimetric curves. These peaks are much smaller than the main calorimetric peaks and precede them, appearing as shoulders on the main peaks.

Fig. 2 plots the integrals of the rate curves presented in Fig. 1 and plot the total heats evolved ($kJ\,mol^{-1}$) during the first hour of hydration. Replicate runs indicated negligible differences between heat evolution curves obtained at a given temperature. Reproducibility is due in part to the rapid hydration rates involved; rapid hydration minimizes the accumulation of error. The curves shown in Fig. 2 illustrate that heat evolution becomes very low within an hour even at 5 °C. Unlike the hydration of tricalcium silicate, which exhibits an extended period of diffusionally controlled reaction, tricalcium germanate hydration reaches completion during this period.

Although complete hydration is achieved at every temperature, the amounts of heat evolved show a temperature dependence. For hydration at temperatures between 5 and 25 °C, the effect is relatively small. The maximum heat evolved is approximately 165 $kJ\,mol^{-1}$ and this occurs for hydration at 25 °C. Fig. 2 also indicates the total heat evolved at temperatures between 25 and 45 °C is constant. However, the time required to attain complete hydration varies inversely with temperature over this range; complete hydration is achieved more slowly at 45 °C than at 25 °C. However, all the reactions reach completion within 0.75 h. The total heat evolved decreases for hydration at temperatures above 45 °C. The largest decrease occurs between 45 and 55 °C. A further decrease in the total heat evolution is minor above 55 °C. The total heats evolved for complete reaction

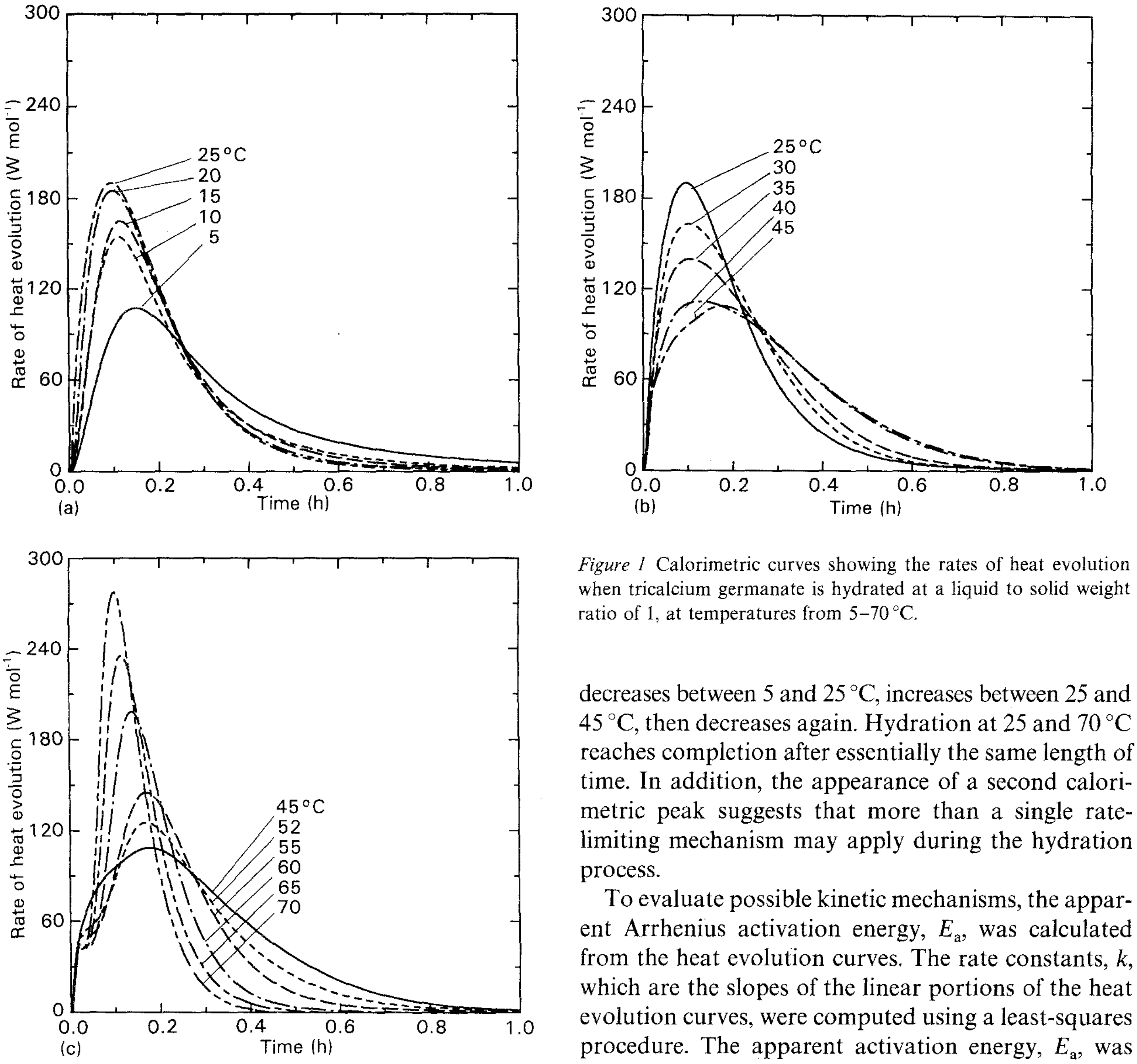


Figure 1 Calorimetric curves showing the rates of heat evolution when tricalcium germanate is hydrated at a liquid to solid weight ratio of 1, at temperatures from 5–70 °C.

decrease from 160 kJ mol^{-1} at 45 °C to about 130 kJ mol^{-1} at 70 °C. The decrease in the total heat evolved initiates at 52 °C, and it is at this temperature that a shoulder appears on the main hydration peak, Fig. 1.

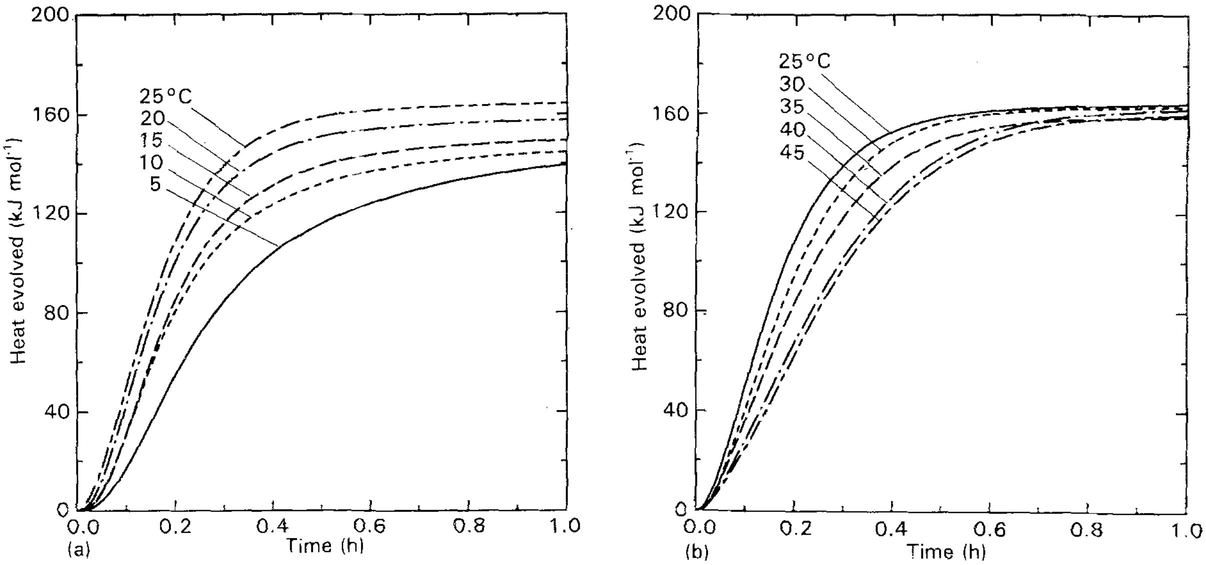
Between 45 and 70 °C, the time at which hydration reaches completion again decreases with increasing temperature. In spite of a diminution in the total heat evolved, the time to complete reaction decreased with increasing hydration temperature. At 70 °C the hydration reaction reaches completion in approximately 0.25 h.

In one sense, the kinetics of tricalcium germanate hydration appear to be less complex than those of tricalcium silicate hydration. Unlike tricalcium silicate hydration, an induction period is not observed even for tricalcium germanate hydration at 5 °C. Unreacted tricalcium germanate could not be observed by X-ray diffraction in the specimens immediately after their removal from the calorimeter. Thus, in contrast to the hydration of tricalcium silicate [14], a diffusionally controlled period in which tricalcium germanate is slowly consumed is not observed. In spite of these, tricalcium germanate hydration is complex. The time required for heat evolution to reach completion decreases between 5 and 25 °C, increases between 25 and 45 °C, then decreases again. Hydration at 25 and 70 °C reaches completion after essentially the same length of time. In addition, the appearance of a second calorimetric peak suggests that more than a single rate-limiting mechanism may apply during the hydration process.

To evaluate possible kinetic mechanisms, the apparent Arrhenius activation energy, E_a, was calculated from the heat evolution curves. The rate constants, k, which are the slopes of the linear portions of the heat evolution curves, were computed using a least-squares procedure. The apparent activation energy, E_a, was determined graphically by plotting log k against $1/T$ and applying the Arrhenius equation

$$\log k = \log A - \frac{E_a}{2.303RT} \qquad (2)$$

Fig. 3 plots the rate constants obtained against the inverse temperature (K). No single value of the activation energy applied over the temperature range of interest. Rather three domains are observed. It is possible to calculate apparent activation energies for two of these, 5–25 and 45–70 °C. The intermediate temperature region from 25–45 °C exhibits transitional behaviour. This is the temperature range where the rates of hydration actually decrease with increasing temperature. An apparent activation energy of 17.6 kJ mol^{-1} was calculated for the low-temperature region, while a value of 42.5 kJ mol^{-1} was calculated for the higher temperatures. This analysis again suggests that more than a single kinetic mechanism governs the hydration of tricalcium germanate. To establish the occurrence of other temperature-dependent phenomena accompanying hydration, limited analyses of the variations in solution chemistry were carried out, the compositions of the hydration products were determined, the unit cell for calcium germanate hydrate determined, and variations in hydration product microstructure were observed.



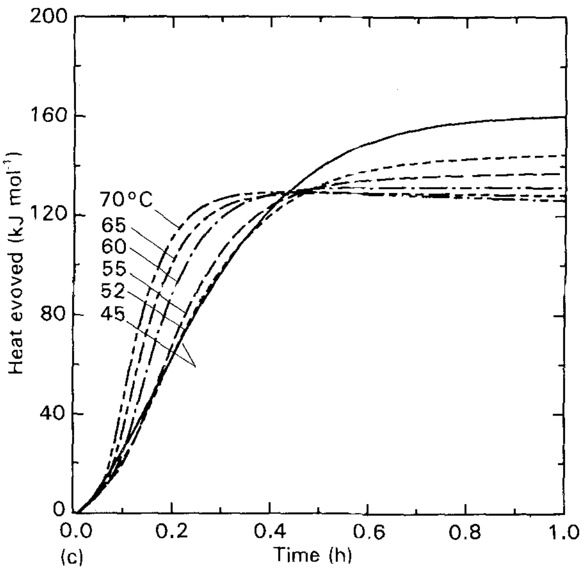


Figure 2 Heat evolution curves for the hydration of tricalcium germanate obtained by integrating the data in Fig. 1. For hydration temperatures below 52 °C, the total heat evolved for complete reaction is an approximately constant value of 160 kJ mol^{-1}. At hydration temperatures of 52 °C and above, total heats of hydration decrease with increasing hydration temperature.

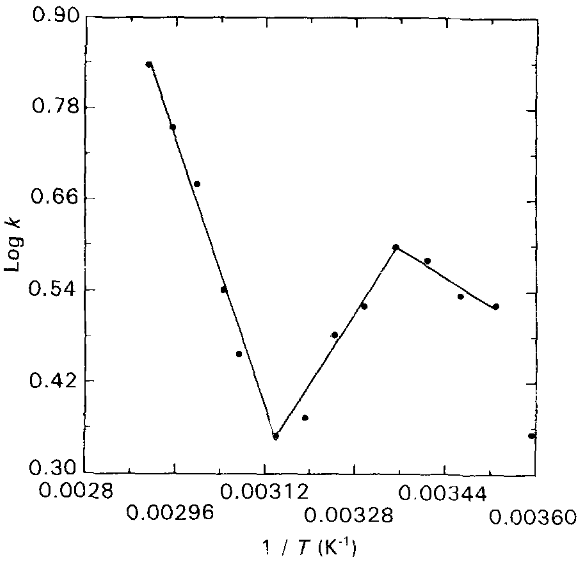


Figure 3 A plot of the apparent Arrhenius energy for the hydration of tricalcium germanate. It was not possible to calculate a single apparent activation energy for the hydration process.

3.2. Solution chemistry

Variations in solution pH were determined at 25 and 70 °C at a water to solid ratio of 30, Fig. 4. Both solutions reach steady-state conditions. The pH values attained are assumed to represent invariant conditions; hydration has reached completion within the times shown in Fig. 2b and c and both calcium hydroxide and calcium germanate hydrate are present. The variations in pH at 25 °C are very similar to those observed during the hydration of tricalcium silicate and are characterized by a rapid increase in pH followed by a period when the pH decreases. After about 0.6 h, the pH reaches an equilibrium value near 12.6. This suggests that the solution becomes supersaturated with respect to $Ca(OH)_2$ and that its subsequent precipitation reduces the solution pH to 12.6. A maximum in pH is observed after about 6 min hydration, suggesting the onset of $Ca(OH)_2$ precipitation to initiate at this time. The variation in pH observed at 70 °C does not indicate a supersaturation event. The pH rises reaching a steady state value of 11.25 after about 36 min hydration. The lower value observed at 70 °C is in accord with the retrograde solubility of $Ca(OH)_2$.

3.3. Hydration product compositions

Thermal gravimetry was used to determine the compositions of the products which formed as a result of tricalcium germanate hydration. X-ray diffraction indicated the presence of calcium hydroxide and a phase of unknown composition which had a pattern similar to that of calcium germanate hydrate reported by Guyader and Lang [8]. Samples which had been fully hydrated samples at 5, 35 and 70 °C were dried at 90 °C for 16 h. These samples were heated to 1000 °C at 10 °C min^{-1} and the percentage weight loss recorded. Fig. 5 shows the weight loss characteristics. There is a relatively rapid loss in weight from 90 to about 200 °C followed by a range of reduced loss between 200 and about 400 °C. The onset of an abrupt

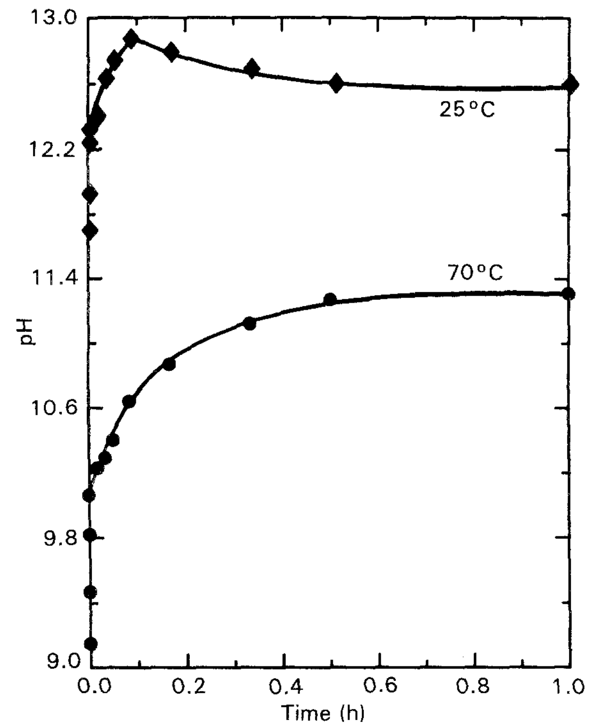


Figure 4 The variations in solution pH during $3CaO \cdot GeO_2$ hydration at 25 and 70 °C at a liquid to solids ratio of 30.

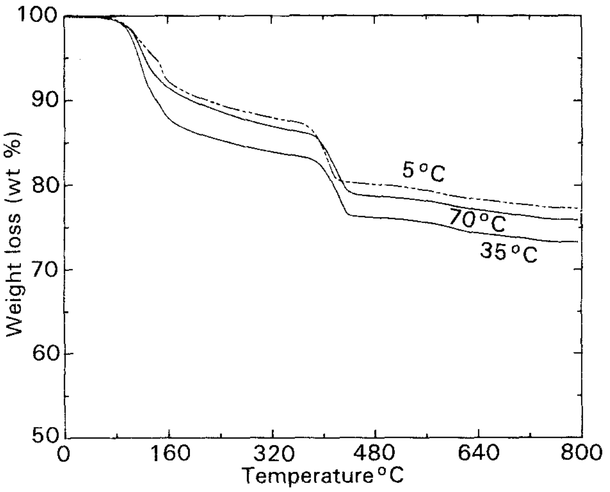


Figure 5 Thermal gravimetric curves for calcium germanate hydrate formed at 5, 35, and 70 °C. The hydrates formed at these temperatures appear to be virtually identical.

loss in weight occurs at about 400 °C. Above about 450 °C, subsequent loss in weight is small. In calculating the compositions of the hydration products, it is assumed that the weight changes initiating at about 400 °C are due to the loss of water from calcium hydroxide and that the loss in weight at lower temperatures is the result of dehydration of calcium germanate hydrate. Thus, composition of calcium germanate hydrate was calculated according to Equation 1. Table I lists the hydration temperatures, and the calculated values of x and n.

The calcium germanate hydrate has a calculated Ca : Ge ratio which increases from 1.59 at 70 °C to 1.68 at 5 °C. These values are close to the value of 1.5 previously observed [1, 3] but substantially lower than the ratio of 2.5 reported by Guyader and Lang [8].

TABLE I Product stoichiometries

Temperature (°C)	x	n
5	1.32	2.37
35	1.36	3.27
70	1.41	2.63

The values obtained for n, the number of waters of hydration in calcium germanate hydrate, are more variable. These values range from about 2.4–3.3, suggesting that a reasonable value is 3.

3.4. Unit cell of calcium germanate hydrate

Powder X-ray diffraction patterns for the hydration products of $3CaO \cdot GeO_2$ are dominated by the intensities of the $Ca(OH)_2$ peaks. Both TGA and XRD analyses confirm that it is present at all temperatures. In addition, XRD analysis demonstrated that the relative intensities of the $Ca(OH)_2$ peaks do not show a temperature dependence. On the other hand. calcium germanate hydrate diffraction peaks are generally low in intensity. However, the intensities observed are adequate to allow comparison of diffraction patterns obtained for specimens hydrated at the various temperatures. Comparison of peak positions and peak intensities did not indicate any temperature-dependent variations in the hydrate.

The diffraction patterns obtained for the calcium germanate hydrate produced in this study were compared to those for calcium germanate hydrates reported in the literature [4–8]. The best fit was to the data of Guyader and Lang [8]. Although peak positions have been reported, the unit cell of calcium germanate hydrate had not been established. Accordingly, the unit cell dimensions were calculated based on the refinement of 24 diffraction peaks (Table II). The calcium germanate hydrate produced at 45 °C was selected for analysis. All 24 d-values were indexed by five methods [9–13]. The unit cell was found to be monoclinic with a, b, c, and β calculated as 1.851, 1.147, 0.531 nm and 98.10 °, respectively. The methods of Visser [10] and Werner *et al.* [12] indicate twice the volume and length of the c parameter compared to the other methods. However, the smaller unit cell is correct because both the Visser and Werner *et al.* methods had all even numbers for l in $h\ k\ l$ indexing.

3.5. Development of microstructure

Although heat liberation characteristics show three distinct regions of behaviour, the reasons for these differences were not discernible based on the results of thermal analysis or X-ray diffraction. These findings appear to eliminate the possibility that different phases form at low and high temperatures with overlap between 25 and 45 °C. However, there are systematic variations in microstructure which may qualitatively explain the observed kinetic behaviour. Microstructural features shown below have been selected to illustrate the evolution in morphology in the three temperature regimes.

TABLE II *d*-values and intensities

d (nm)	Intensity	*d* (nm)	Intensity	*d* (nm)	Intensity
0.9721	100	0.3874	27	0.3008	7
0.9187	21	0.3709	15	0.2856	34
0.5732	42	0.3541	13	0.2821	21
0.5386	80	0.3499	6	0.2654	26
0.5261	9	0.3437	5	0.2627	14
0.4775	30	0.3233	22	0.2534	6
0.4479	6	0.3109	4	0.2523	7
0.4025	44	0.3051	7	0.2383	6

Figure 6 Calcium germanate hydrate formed at 5 °C is typified by tightly matted fibres.

Fig. 6 shows the microstructure of calcium germanate hydrate formed at 5 °C. The morphology of calcium germanate formed at this temperature is characterized by a felt-like mat of tightly intertwined fibres. Two fibre types are present. The background is composed of interwoven individual fibres of indeterminant length, while multifilimentary fibre strands are seen in the centre of the micrograph. The lengths of these strands were observed to exceed 30 μm. Thermal and X-ray analyses showed calcium hydroxide to be present but it could not be identified on any of the fracture surfaces on which observations were made. Fig. 7 shows a microstructure typical of that observed at 25 °C. The fibrous habit retained by the fibre network is more open. Only individual fibres are observed at this temperature and their lengths appear to be shorter. Calcium hydroxide could not be observed. Fig. 8 shows morphological development at 35 °C. Compared to lower temperatures, the fibres which form are shorter and somewhat larger in cross-section. In contrast to the general morphologies at lower temperatures, the microstructure is characterized by a distribution of spherically shaped bundles of woven hydrate fibres. This feature is suggestive of the retention of the spatial relationship with the parent tricalcium germanate particles and it is not observed at the higher or the lower temperatures. Calcium hydroxide crystals are observed at this temperature. The spatial relationship in which calcium germanate hydrate exhibits a general pseudomorphic relationship with the parent tricalcium germanate occurs over the temperature range in which the rate of hydration decreases with increasing temperature. This suggests a relationship similar to that observed in the hydration of tricalcium silicate. The formation of calcium silicate hydrate in the vicinity of the surface of the hydrating tricalcium silicate grains results in extended periods of slow reaction [15]. Such a lengthy period of diffusion control is not observed for tricalcium germanate hydration because the microstructural analogy is incomplete; calcium germanate hydrate is far more fibrous than calcium silicate hydrate and, as a consequence, is less effective as a diffusion barrier. In addition, while the hydrolysis of both tricalcium silicate and tricalcium germanate produce calcium ions, the germanium oxide produced in hydrolysis is far more soluble than hydrous silicate species produced. Therefore, there is a much lower driving force for hydrate formation close to the parent grains.

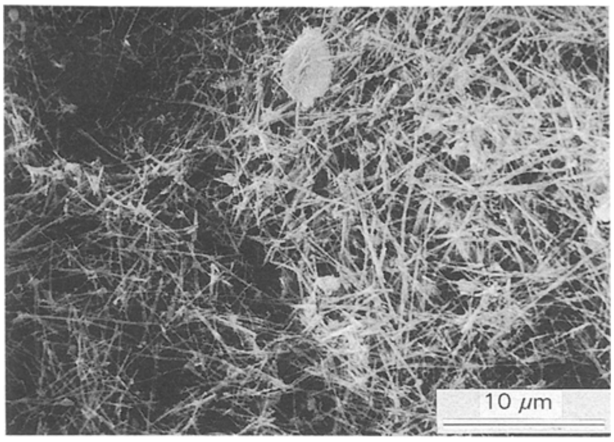


Figure 7 Calcium germanate hydrate forms as a loose network of individual fibres at 25 °C.

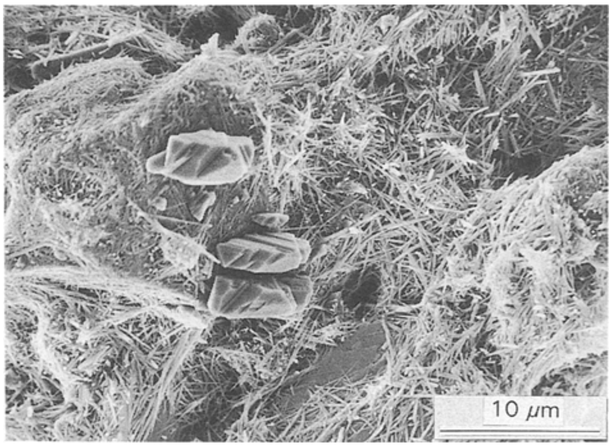


Figure 8 Calcium hydroxide can be observed in association with fibrous calcium germanate hydrate at 35 °C.

The microstructure observed at 45 °C is reminiscent of that at 5 °C (Fig. 6) and is characterized by densely interwoven fibres, Fig. 9a. Relatively large calcium hydroxide grains are observed and these seem to engulf calcium germanate hydrate fibres, Fig. 9b. In some regions, aligned multifilimentary fibre strands are observed to grow to lengths which exceed 50 μm or more. In view of the fact that complete hydration is achieved in about 45 min at this temperature, the

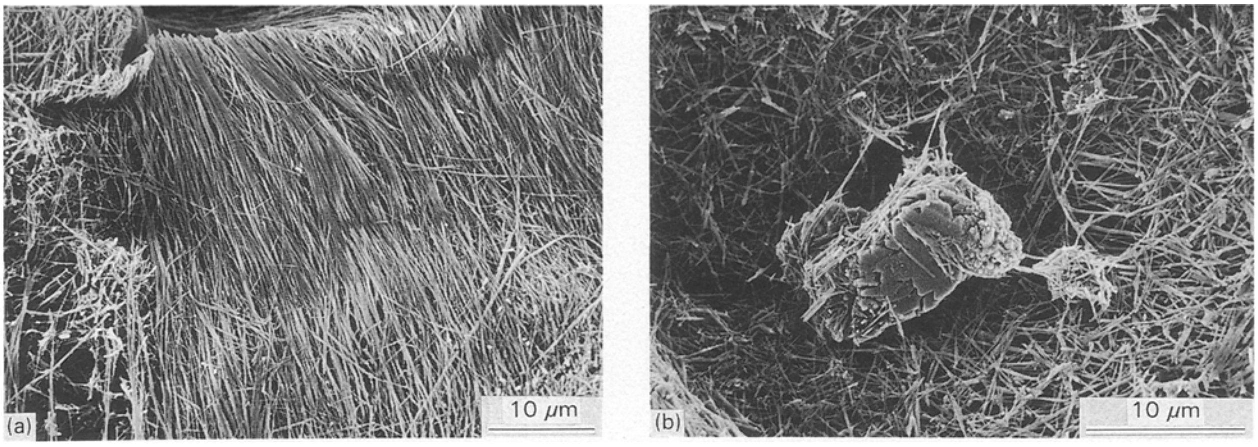


Figure 9 (a) Regions of oriented fibres of calcium germanate hydrate and (b) intergrowths of calcium hydroxide and calcium germanate hydrate, are present at 45 °C.

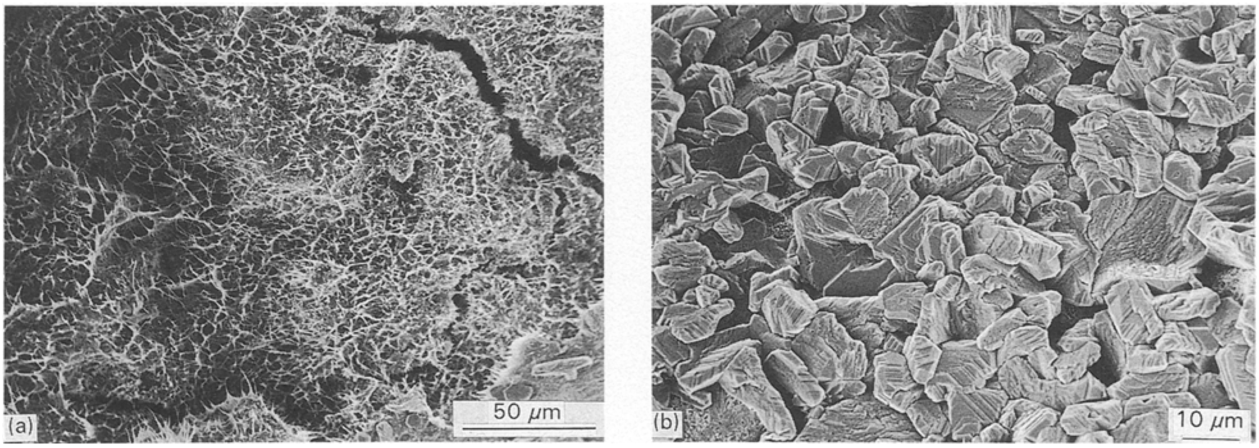


Figure 10 (a) Distinct region of reticulated calcium germanate hydrate and (b) distinct regions of masses of calcium hydroxide crystallites, form at 55 °C.

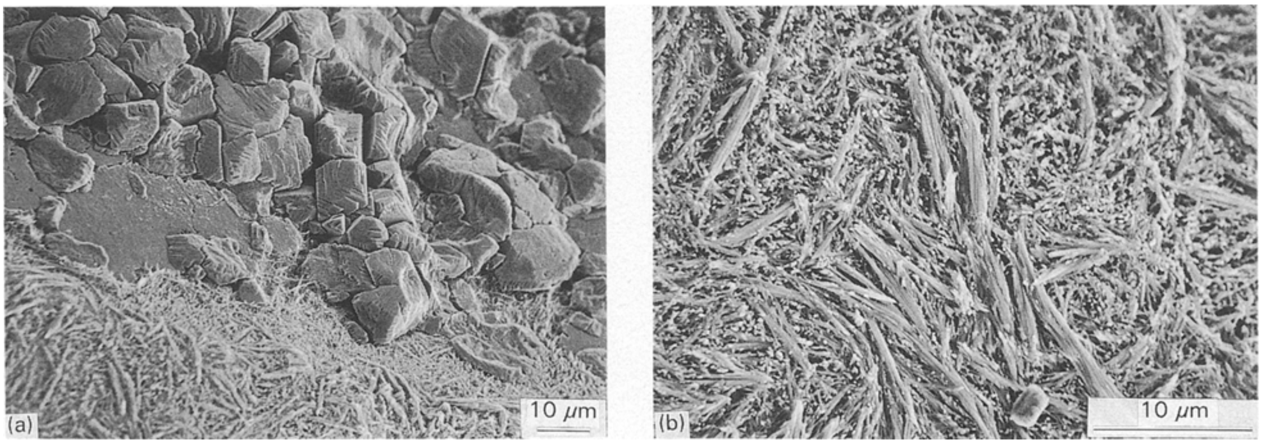


Figure 11 (a) Masses of calcium hydroxide crystallites are also present at 60 °C, while the aspect ratio of calcium germanate hydrate formed is much lower than at the other temperatures (b) (see especially Figs 10 and 12).

average linear growth rate of these fibres exceeds 1 μm min^{-1}. Microstructural changes between 45 and 55 °C are profound. Calcium germanate hydrate formed at 55 °C is no longer fibrous but exhibits a reticulated microstructure, Fig. 10a. Massive regions of calcium hydroxide are also observed at this temperature, Fig. 10b. Massive regions of calcium hydroxide are present in the microsturcture developed at 60 °C, Fig. 11a. However, the microstructure of the calcium germanate hydrate is characterized by fibrous bundles of relatively short fibres, Fig. 11b. This behaviour is in direct contrast to the microstructure observed at 70 °C, Fig. 12. The calcium germanate hydrate and calcium hydroxide which form at this temperature do

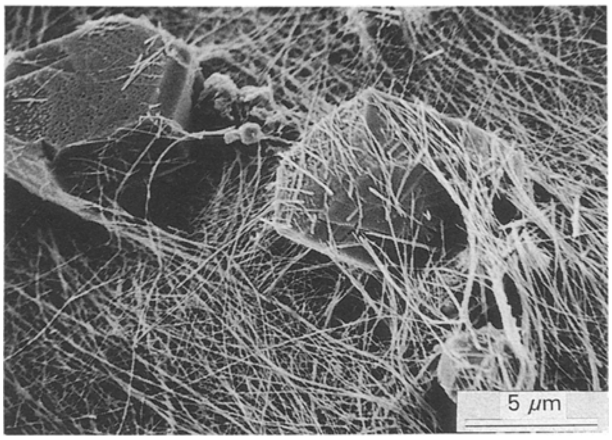


Figure 12 Fibrous calcium germanate hydrate formed at 70 °C; a region where it is engulfed by calcium hydroxide is shown.

so in close association. The calcium germanate again forms as high aspect ratio fibres at 70 °C. The micrograph shows a cluster of fibres to be engulfed by growing crystals of calcium hydroxide, suggesting that a substantial amount of calcium germanate hydrate has formed prior to the growth of the calcium hydroxide crystals.

While predominant morphology of the calcium germanate hydrate is fibrous, temperature-dependent variations in its morphology and spatial distribution and its relationship with calcium hydroxide occur. In a qualitative sense these variations correlate with the rate of hydration of tricalcium germanate.

4. Conclusion

Analysis of the kinetics of tricalcium germanate hydration over the range of temperature from 5–70 °C indicates that hydration rapidly reaches completion. Unlike hydration of tricalcium silicate, an induction period and a lengthy period of slow hydration are not observed. In spite of the absence of these complicating kinetic phenomena, tricalcium germanate hydration is complex and a single value for the apparent activation energy capable of describing the hydration kinetics could not be determined. The composition of calcium germanate varies slightly with temperature. The Ca:Ge ratio decreases from 1.68 to 1.59 over the temperature range 5–70 °C. The unit of calcium germanate hydrate is monoclinic. The three cell parameters, *a*, *b*, *c*, and β were calculated to be 1.851, 1.147, 0.531 nm and 98.10°. The predominant microstructure of calcium germanate hydrate is fibrous; however, temperature-dependent variations are observed. In spite of the microstructural variations with temperature, the evidence suggests that there are no major compositional changes in the calcium germanate hydrate that forms over this temperature range.

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