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EVALUATION OF PHASES IN A HYDROTHERMALLY TREATED CaO–SiO_2–H_2O SYSTEM

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Abstract

The evolution of hydration products with reaction time in a hydrothermally cured CaO–SiO_2–H_2O system, when using quartz of different fineness, was investigated by means of thermal, X-ray diffraction and wet chemical techniques. A combination of second derivative differential thermal-, first derivative thermogravimetric- and the equivalent differential thermal- and thermogravimetric curves provided more critical information about the nature of phases formed than X-ray diffraction alone. Phenomena including overlapping dehydration reactions and interactions of phases during the thermal experiment are discussed and illustrated by examples.

Keywords: derivative thermal curves, hydrothermal curing, 11 Å tobermorite, xonotlite

Introduction

Nearly 50 years ago, Kalousek was one of the first to study the phases produced in autoclaved or hydrothermally cured lime-silica [1] and cement-silica [2] systems by employing thermal analysis techniques. Since then, numerous investigations have been conducted on the CaO–SiO_2–H_2O system under hydrothermal conditions due to its importance in relation to commercially available construction materials [3, 4].

While DTA-TG has been employed extensively to study the nature of calcium silicate hydrates (C–S–Hs) formed in hydrothermally cured CaO–SiO_2–H_2O systems, information on the use of a combination of: differential thermal (DT), thermogravimetric (TG), second derivative differential thermal (DDT) and first derivative thermogravimetric (DTG) curves appears to be lacking. Furthermore, the possibility of overlapping dehydration reactions and interactions amongst the phases during the thermal experiment appears to have received only little attention [3, 4].

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The present paper addresses some of these issues and illustrates how a combination of DT, TG, DDT and DTG curves can be used effectively to study the evolution of hydration products with reaction time in a hydrothermally cured CaO–SiO_2–H_2O system, when using quartz of different fineness.

Experimental

The method employed in this study was based on that of Kalousek [5]. The starting materials were mixtures of CaO (prepared by calcination of reagent grade $CaCO_3$ at 1050°C for 5 h) and ground quartz (99.8% SiO_2 for fine quartz with a median particle size less than 8 μm, and 99.0% SiO_2 for coarse quartz with median particle size less than 35 μm, from Ballarat, Victoria (Australia)). Details of slurry preparation and hydrothermal treatment have been given elsewhere [6]. Briefly, two slurried mixtures were prepared, using a water to total solids ratio of 5 and at a bulk C/S composition of 0.8 with fine and coarse quartz respectively. The resulting slurry was divided among 6 small Parr bombs and placed in a temperature-controlled oven set at 100°C. These bombs were heated to 180°C in 40 min and removed from the oven upon completion of the 40 min temperature ramp from 100 to 180°C,– designated 0 h –, then after 1, 2, 4, 9 and 23 h at 180°C. Samples were vacuum dried at 60°C for a minimum of 24 h then ground for 4 min using a mortar and pestle followed by an additional vacuum drying period.

The hydration products with reaction time were evaluated as follows:
a) DTA-TG using the TA instruments SDT 2960 simultaneous DTA-TGA analyser at a heating rate of 10°C min^{-1} under flowing nitrogen (100 mL min^{-1}) from 60 to 1100°C. Sample sizes were between 15 to 20 mg and packed into a Pt–Rh crucible with 20 taps. All curves were evaluated using the TA instruments' software. Two-point rotations were carried out for all DT curves as described previously [7]. Mass losses were determined by employing both TG and DTG curves as described previously [7]. DDT curves were used for peak temperature determinations [8].
b) The amount of acid-insoluble residue (AIR) served as a measure of quartz remaining unreacted. Experimental details are given elsewhere [9]. Data from a) and b) were used to estimate the following:

- Total combined water (H_2O) content (loss on ignition (LOI) between 60 to 1050°C).
- Combined H_2O content in C–S–Hs (combined H_2O in C–S–H); this was regarded as being identical with the LOI after making a correction for the portlandite ($Ca(OH)_2$) present taking into consideration that each one mole of free CaO is accompanied by one free mole of non-evaporable H_2O.
- It is noteworthy that mass losses attributed to $Ca(OH)_2$ may be subject to overlap as C–S–Hs are known to dehydrate gradually and variably over a wide temperature range up to ~800°C [10]. Additionally, the possibility of alpha-dicalcium silicate hydrate (α-C_2SH) presence also interferes with the determination of $Ca(OH)_2$ amount.
- Molar ratio C/S in the C–S–Hs (estimated C/S ratio).

- All specimens were examined by X-ray diffraction (XRD) using a Siemens D-5000 diffractometer and CuK_α radiation at a scanning speed of 1.2° min^{-1} between $2\theta=2$ to 80° and an 8 s count time per step. Selected specimens were heated for 1.5 h at specified temperatures in the range of 500 to 900°C in air followed by cooling in a desiccator over silica gel, and phase changes were investigated by XRD at a scanning speed of 1.8° min^{-1} between $2\theta=5$ to 65° and a 3 s count time per step.

Results and discussion

DT curves for samples prepared with coarse and fine quartz are shown in Figs 1 and 2, respectively. Data for 'AIR', estimated 'C/S ratio' and 'combined H_2O in C–S–H' are depicted in Figs 3a–c, respectively. From these the following are evident:

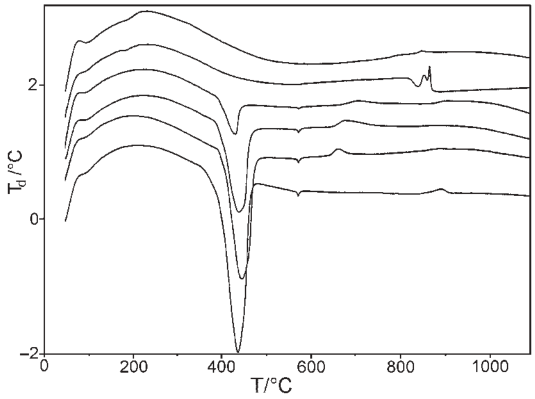

Fig. 1 DT curves for specimens prepared with coarse quartz hydrothermally cured for (bottom to top) 0, 1, 2, 4, 9 and 23 h

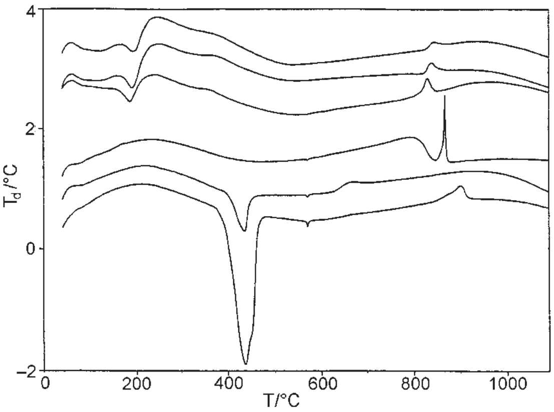

Fig. 2 DT curves for specimens prepared with fine quartz hydrothermally cured for (bottom to top) 0, 1, 2, 4, 9 and 23 h

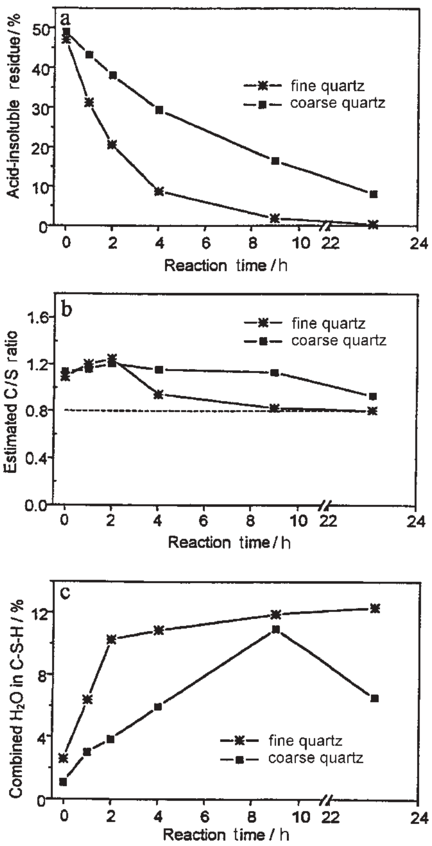

Fig. 3 Percent acid-insoluble residue (a), estimated C/S ratio (b) and percent combined H_2O content (c) in C–S–H *vs.* reaction time for samples prepared with fine or coarse quartz

1. The rate of portlandite consumption, to form C–S–Hs, was retarded when coarse quartz was used due to the lower reactivity/solubility of the latter. Portlandite was still present after 4 h of hydrothermal treatment, in contrast it was only present up to 1 h when using fine quartz. This is also evident from both the ‘AIR’ (Fig. 3a) and the estimated ‘combined H_2O in C–S–H’ (Fig. 3c) data which clearly reflect the lower reactivity of coarse quartz.

Closer inspection of the endotherm, ascribed to $Ca(OH)_2$, reveals a distinctive ‘peak asymmetry’. DDT curves clearly revealed this peak asymmetry to be due to a double endotherm after 0 to 2 h and after 0 h when coarse or fine quartz were used respectively, an example is given in Fig. 4. This double endotherm may be due to the presence of α-C_2SH^4 in addition to $Ca(OH)_2$ or a particle size effect [11] due to portlandite. α-C_2SH could not be identified by XRD with certainty suggesting that if present it was not sufficiently crystalline.

2. DTA results reveal the presence of exotherms below ~750°C for up to 4 h when coarse quartz was used and for up to 1 h only for fine quartz. A distinctive shift

of exotherms to the ~800 to 900°C region is evident after 9 and 2 h for coarse and fine quartz, respectively. The DT curve reveals two exothermic peaks after 9 h when coarse quartz was used (Fig. 1). In contrast, when fine quartz was used and after 2 h, the dominant feature in the DT curve is a prominent exotherm (Fig. 2) and a small shoulder on the low temperature side of this exotherm (Fig. 5). The presence of double exotherms indicates that at least two types of C–S–Hs were present [3, 4].

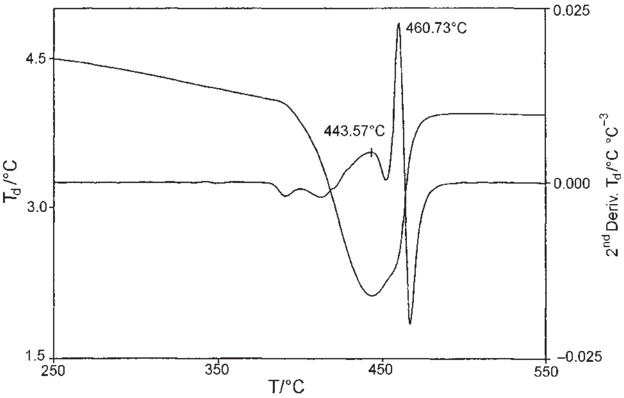

Fig. 4 DT and DDT curves after 1 h of hydrothermal treatment when coarse quartz was used

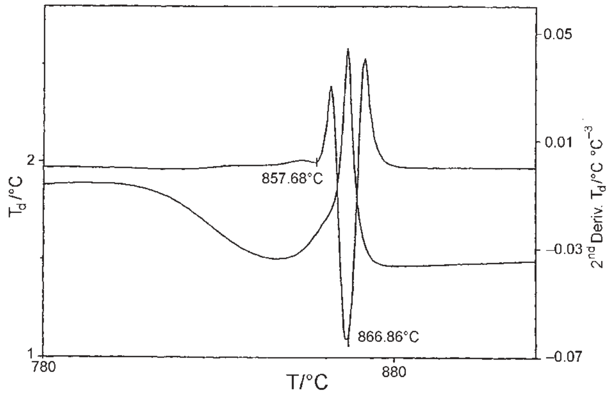

Fig. 5 DT and DDT curves after 2 h of hydrothermal treatment when fine quartz was used

As exotherms are due to recrystallization processes or the emergence of new phases, the low temperature exotherms in the present examples are believed to represent recrystallization of decomposed or dehydrated C–S–Hs into larnite (β-C$_2$S) and possibly also into wollastonite (β-CS) while the exotherms in the ~800 to 900°C region are predominantly due to the recrystallization into β-CS.

Samples prepared with coarse quartz and hydrothermally cured for 1 and 2 h were heated for 1.5 h at 500 and 700°C. XRD examination revealed that β-C$_2$S had formed by 700°C. β-C$_2$S was not detected in specimens heated at 500°C. After 4 h of hydrothermal curing, specimens heated at 700°C contained β-C$_2$S and when heated at 900°C, β-CS had also formed as a minor phase. Reflections due to quartz were present in all specimens examined by XRD. In contrast, samples prepared with fine quartz and hydrothermally cured for 2 h manifested significantly stronger peaks due to β-CS than due to β-C$_2$S after heating at 900°C. After 4 h of hydrothermal curing, specimens heated at 900°C contained peaks due to β-CS only. Once again, reflections due to quartz were present in all specimens examined by XRD.

Mitsuda *et al.* [12] have reported the formation of β-C$_2$S for C–S–Hs with C/S ratio greater than or equal to 1.3, while Stade [13] detected β-C$_2$S also from C–S–H specimens with C/S ratio of 1.2. The formations of both β-CS and β-C$_2$S have been observed for C–S–Hs with C/S ratios between 1.5 and 1.2, while C–S–H specimens with C/S ratios equal to or less than 1.0, formed β-CS only [12–14]. For specimens of the present investigation the exotherms therefore indicate that lime-rich C–S–Hs persisted longer when coarse quartz was used. This is also manifested by the variation in the estimated C/S ratio with reaction time depicted in Fig. 3b.

It is interesting to note that the low-temperature exotherm, for samples prepared with coarse quartz, shifted from 660°C to 704°C, after 1 to 4 h of hydrothermal treatment. Additionally, DDT curves revealed two discernible exotherms after 1 and 2 h of hydrothermal treatment in this temperature region, as is illustrated in Fig. 6. It has been shown that the initial C–S–H structures are variable [12–14]; it follows that the energy required for their dissociations will be different and the temperatures at which dissociations and recrystallizations or formations of new phases begins will also differ. The multiple exotherms observed and their shift in temperature, as revealed by DTA, thus infers the presence of several C–S–H structures, which changed with reaction time. In contrast, XRD examination of specimens hydrothermally cured for up to 4 h and 1 h when coarse and fine quartz were used respectively revealed similar C–S–H patterns except for the noted decrease in reflections due to quartz and portlandite. These observations emphasize that, due to the lack of long-range order [15] in poorly-crystalline C–S–Hs, conventional XRD methods are not as sensi-

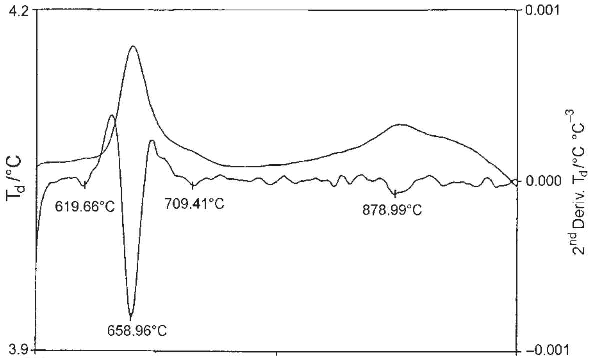

Fig. 6 DT and DDT curves after 1 h of hydrothermal treatment when coarse quartz was used revealing a double exotherm

tive in revealing structural differences while DTA appears to be more sensitive in revealing possible structural differences.

The authors would like to point out, however, that interpretations can be difficult as there exists the possibility of interactions amongst phases during the thermal experiment. For example, DT curves reveal a double exotherm between ~850 to 950°C after 0 h of hydrothermal treatment (Figs 1 and 2). This double exotherm is considered to be due to the formation of new phases from interactions between CaO, through the decomposition of $Ca(OH)_2$, and quartz and possibly also C–S–Hs present in the sample.

That such phenomena can occur was confirmed by heating a mixture of $Ca(OH)_2$ (37% by mass) and fine quartz (63% by mass), homogenized using a mortar and a pestle, to 1100°C. The resulting DT and DDT curves, depicted in Fig. 7, reveal exotherms at ~642, 869 and 909°C. Additionally, it has been noted that the presence of CaO, which is expected to form from the decomposition of $Ca(OH)_2$, may interact with the dehydrating C–S–Hs, raising the effective C/S ratio and thus facilitate β-C_2S formation [10]. From this discussion it is clear that in the presence of $Ca(OH)_2$, interactions amongst phases during the thermal experiment are possible and thus can complicate the interpretation of the thermal data.

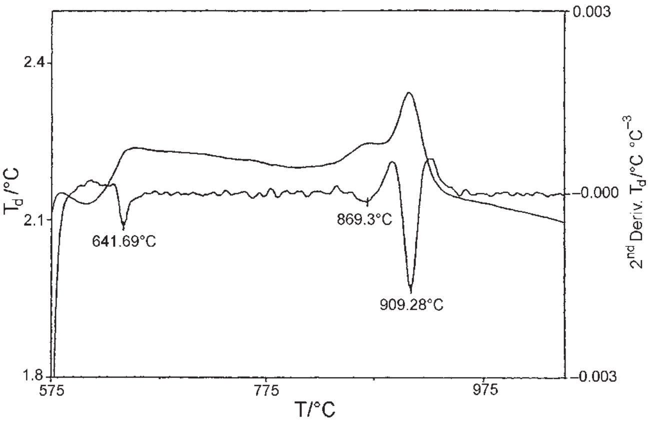

Fig. 7 DT and DDT curves of a (37% by mass) $Ca(OH)_2$ - (63% by mass) fine quartz mixture heated to 1100°C

3. Presence of 11 Å tobermorite ($C_5S_6H_5$) was evident after 4 h when using fine quartz. Its crystallinity improving with continued reaction time. This is manifested by: the distinctive, large endotherm at ~188°C after 4 h increasing to ~200°C after 23 h; the exotherm between ~360 to 370°C due to the crystallization into 9 Å tobermorite [16, 17] and the small exotherm at ~840°C due to the crystallization into β-CS decreasing in size from 4 to 23 h.

In contrast when coarse quartz was used, only poorly crystalline $C_5S_6H_5$ was detected after 9 h, its crystallinity however, improving significantly after 23 h as revealed by XRD, a consequence of more quartz having reacted (Fig. 3a). After 23 h xonotlite (C_6S_6H) had also formed, its presence being manifested by a distinctive endothermic response peaking at ~760°C (Fig. 8) due to dehydroxylation, in addition to the noted decrease in the 'combined water in C–S–H' (Fig. 3c).

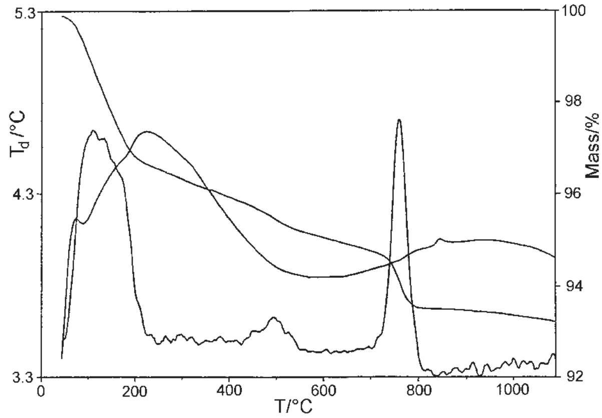

Fig. 8 DT, TG and DTG curves after 23 h of hydrothermal treatment when coarse quartz was used

It has been reported that $C_5S_6H_5$ is unstable relative to C_6S_6H at 180°C [18] and that 'the slowness of decomposition of $C_5S_6H_5$ into C_6S_6H gives the rate-determining stage on the reaction between quartz and lime' [19]. The fact that in the present investigation, $C_5S_6H_5$ crystallinity improved significantly after 23 h suggests that C_6S_6H had formed predominantly as a companion phase rather than being a result of $C_5S_6H_5$ decomposition. This then suggests that at least two types of C–S–H species must have been present. Support for this notion comes from the presence of the two distinct exotherms (Fig. 1) after 9 h of hydrothermal treatment. XRD did not provide this type of information further highlighting the usefulness of thermal analysis.

4. Differences in the dehydration behaviour for samples prepared with fine and coarse quartz were also evident, and this will be the subject of a future publication.

The examples presented in this paper have clearly demonstrated the advantages of employing both DT and DDT curves in the evaluation of thermal effects. By employing DT and DDT curves in combination, more accurate peak temperature determinations can be made and additional information is gained because of the improvement in resolution. The use of DT and DDT curves in combination should prove useful in many other fields of research employing DTA-TG.

Conclusions

From the data presented in this paper we conclude the following:

- The second derivative differential thermal curve provides more detailed information than the equivalent differential thermal curve alone. The second derivative differential thermal curve provides a means for detecting multiple endothermic or exothermic responses.

- The determination of portlandite amount from TG and DTG data is subject to overlap due to calcium silicate hydrate dehydration reactions occurring concurrently.
- In studies pertaining to the hydrothermally cured CaO–SiO_2–H_2O system, thermal analysis in combination with XRD can provide more detailed information about the nature of phases formed than XRD alone.
- In the presence of portlandite, interactions amongst phases during the thermal experiment are possible and thus can complicate the interpretation of the thermal data.
- The use of fine quartz resulted in the formation of crystalline 11 Å tobermorite after 4 h of hydrothermal treatment. This phase increased in crystallinity with reaction time. In contrast, the slower release of silicate anions from coarse quartz prolonged the presence of lime-rich C–S–Hs and resulted in the formation of poorly crystalline 11 Å tobermorite after 9 h. Xonotlite is believed to have formed predominantly as a companion phase, rather than being a result of 11 Å tobermorite decomposition, after 23 h of hydrothermal treatment.

References

1 G. L. Kalousek, J. Amer. Concr. Inst., 51 (1955) 989.
2 G. L. Kalousek, J. Amer. Concr. Inst., 50 (1954) 365.
3 J. M. Coldrey and M. J. Purton, J. Appl. Chem., 18 (1968) 353.
4 M. J. Purton, J. Appl. Chem., 20 (1970) 293.
5 G. L. Kalousek, J. Am. Ceram. Soc., 40 (1957) 74.
6 D. S. Klimesch and A. Ray, Cem. Concr. Res., 28 (1998) 1109.
7 D. S. Klimesch and A. Ray, Thermochim. Acta, 289 (1996) 41.
8 D. S. Klimesch and A. Ray, Thermochim. Acta, 307 (1997) 167.
9 D. S. Klimesch and A. Ray, Adv. Cem. Res., 9 (1997) 157.
10 Y. Okada, K. Sasaki, B. Zhong, H. Ishida and T. Mitsuda, J. Amer. Ceram. Soc., 77 (1994) 1319.
11 M. I. Pope and M. D. Judd, Differential Thermal Analysis a Guide to the Technique and its Applications, Heyden & Son Ltd., London 1977, p. 24.
12 T. Mitsuda, S. Kobayakawa and H. Toraya, 8th Proc. Int. Congr. Chem. Cem., 3 (1986) 173.
13 H. Stade, Z. Anorg. Allg. Chem., 470 (1980) 69 (in German).
14 H. Stade and W. Wieker, Z. Anorg. Allg. Chem., 466 (1980) 55 (in German).
15 D. Viehland, J. F. Li, L. J. Yuan and Z. Xu, J. Am. Ceram. Soc., 79 (1996) 1731.
16 R. Gabrovsek, B. Kurbus, D. Müller and W. Wieker, Cem. Concr. Res., 23 (1993) 321.
17 Yu. M. Butt, V. V. Timashev, V. S. Bakshutov, M. K. Grineva and V. V. Ilyukhin, Proc. 3rd ICTA DAVOS, 3 (1971), Birkhäuser Verlag, Basel, 1972, p. 513.
18 K. Speakman, Min. Mag., 36 (1968) 1090.
19 T. Mitsuda, J. Saito and E. Hattori, Proc. 1st Int. Symp. Hydrothermal Reactions, (1982) 823.