Thermochimica Acta, 224 (1993) 241–246
Elsevier Science Publishers B.V., Amsterdam

The use of DTA to determine the effects of mineralizers on the cement–quartz autoclave reactions.
Part 1. Gibbsite addition

E.R. Cantrill [a], M.G. Stevens [a], A. Ray [a,*] and L. Aldridge [b]

[a] *Department of Materials Science, University of Technology, Sydney, P.O. Box 123, Broadway, Sydney, NSW, 2007 (Australia)*

[b] *Australian Nuclear Science and Technology Organisation, Private Mail Bag 1, Menai, NSW, 2234 (Australia)*

(Received 1 December 1992; accepted 5 January 1993)

Abstract

The effect of increasing gibbsite addition on the steam-autoclave-cured cement–quartz reaction was investigated mainly by DTA with additional support from XRD. The products progressed from essentially hydrated calcium silicate [CSH(I)] through a type of hydrogarnet [C_3ASH_4] to hydrated calcium aluminate [C_3AH_6].

INTRODUCTION

High-pressure steam autoclaving is used to cure cementitious materials to give products of higher strength within 8–10 h of manufacture, thus allowing more rapid turnover with less storage requirement for curing than that required by air curing. Properly proportioned and autoclaved products have greater resistance to shrinkage, carbonation, corrosion and chemical leaching.

Autoclaving cement with fine quartz prevents the formation of free lime, $Ca(OH)_2$ [CH][1] and $Ca_3Al_2(OH)_{12}$ [C_3AH_6], both of which can react with carbon dioxide, the former giving $C\bar{C}$ only, the latter resulting in a mixture of $C_3A \cdot C\bar{C} \cdot H_{11}$, $C\bar{C}$, and AH_3 [1, 2]. Autoclaving also results in a more stable form of hydrated calcium silicate, CSH(I), closely related to the mineral 1.13 nm tobermorite, [$C_5S_6H_5$]. Although the CaO–SiO_2 system has been extensively studied, as have the individual cement phases, comparatively few investigations have been made on the commercially manufactured, hydrothermally cured cement–quartz system.

From DTA analysis, Kalousek [3] found that small amounts of alumina entered the tobermorite crystal lattice under autoclaving conditions and

---

* Corresponding author.

[1] Cement chemistry nomenclature: C = CaO, S = SiO_2, A = Al_2O_3, H = H_2O, $\bar{C}$ = CO_2.

modified its properties. The silica in 1.13 nm tobermorite can be substituted by alumina to a maximum Al/(Al + Si) ratio of 0.14 [4]. Milestone et al. [5] observed that Al-rich tobermorite was resistant to high-pressure–high-temperature carbonation in oil-well cement grouts. Sun et al. [6] considered that tobermorite and hydrogarnet [C_3ASH_4] were both important in reducing shrinkage. The rate of tobermorite formation is accelerated by addition of reactive aluminous materials [7]. However, any hydrogarnet formed takes up a relatively high proportion of lime without contributing to any significant bonding [8].

The effect of gibbsite [AH_3] addition on the cement–quartz autoclave reaction was investigated for a cement/silica (C/S) ratio of 50/50. This ratio was chosen because it is similar to those used in industrial autoclaved building products. It ensures full reaction of the cement with a slight excess of unreacted quartz in the final product.

The phase compositions were identified by DTA and measured qualitatively by peak heights from the DTA thermographs. The phases identified were hydrogarnet [C_3ASH_4] shown by an endotherm at 320–360°C [3] and by a weak exotherm at 930°C, CSH(I) by a sharp exotherm at 865°C [3], unreacted quartz [S] by a sharp endotherm at 573°C [9], and C_3AH_6 by an endotherm at 320°C where it loses 4.5 molecules of water, and a second endotherm at 495°C where it loses the remaining 1.5 molecules [10].

EXPERIMENTAL

The raw materials used in this investigation were

Cement:	Type A Ordinary Portland Cement (OPC) from Blue Circle Southern Portland Cement, Berrima Works (NSW).
Silica:	Commercial Minerals Grade 200G ground quartzite from Ballarat, Victoria.
Gibbsite:	alumina trihydrate, commercial grade H337, from Alcoa, Western Australia.

Gibbsite additions of 0%, 2%, 4%, and thereafter of 4% increments were made up to a maximum of 60%. A constant water/(cement + quartz + gibbsite) ratio of 0.36 was used for the preparation of samples of autoclaving. The 50/50 cement/silica (300–400 g) was weighed out into a 500 g glass jar. A total of 25 g, including various amounts of gibbsite, was taken from this premixed cement/quartz blend, then 9 ml of water were added and thouroughly mixed prior to transferring to a 50 mm × 25 mm square polyethylene histology mould.

The moulds were exposed to normal carbon-dioxide-containing atmosphere and left to cure for 16 h under ambient conditions. The samples were then immersed in water for 6 h followed by autoclaving under saturated steam at 0.8 MPa pressure and a temperature of 177°C for 6 h, with a 2 h rise and a 1 h fall in pressure.

A sample for DTA was taken from each specimen after removing the outer 1 mm by filing in order to minimize carbonation contamination. Analyses were conducted using a Rigaku 8008HT thermal analyzer with a micro-DTA head. Approximately 60–70 mg of samples were used for DTA analysis. A sintered 1:1 Al_2O_3/kaolinite mixture was used for reference.

Selected specimens were also examined by XRD using a Philips PW 1729 X-ray generator using cobalt $K\alpha_1$ radiation and scanned with a PW 1840 diffractometer.

RESULTS AND DISCUSSION

The DTA results are presented in Fig. 1 which shows that the predominant phase at 0% gibbsite addition is CSH(I). The large, sharp exotherm at 865°C indicates that alumina from the Portland cement has entered the CSH(I) lattice. Pure Al-free tobermorite shows only a change in baseline in this temperature range [3].

Addition of up to 20% gibbsite results in a progressive reduction in height as well as a progressive shift of this exothermic peak towards higher temperatures. At 20% gibbsite addition, this exotherm is almost negligible in height and lies at a temperature of 885°C, and increase of 20°C.

The amount of unreacted quartz, with a sharp endotherm at 573°C, increases slightly with increasing gibbsite addition indicating that there is some competition between the quartz and gibbsite for the available lime.

Free gibbsite, with an endotherm at 260–270°C, can be detected at 2% addition. As this endotherm is similar in size for 2, 4 and 8% gibbsite additions, it appears that this unreacted material represents a coarse, less reactive fraction of the gibbsite. There is a considerable increase in unreacted gibbsite from 8% to 60% addition, as shown in Fig. 1.

The 325°C endotherm, due to the dehydration of the hydrogarnet C_3ASH_4, appears with approximately 4% gibbsite addition and continues to increase in size with increasing addition of up to 16% gibbsite. Thereafter this phase decreases with increasing gibbsite addition, presumably due to dilution with unreacted gibbsite and to new phases forming.

A minor unidentified endotherm appears at 450°C above 4% gibbsite addition and increases in size up to 36% gibbsite addition. Thereafter this endotherm slowly diminishes, again due to the assumed dilution with unreacted gibbsite.

Another broader endotherm at approximately 505°C appears at the 20% gibbsite level, slowly increasing in size with further gibbsite addition. This endotherm is due to the dehydroxylation reaction of boehmite which is a gibbsite dehydration product [9].

The broad endotherm at 740°C suggests decomposition of scawtite, a calcium silicate carbonate [$C_6S_5\bar{C}H_2$]. The hydrogarnet dehydration residue exotherm at 950°C indicates its conversion to anorthite [CAS_2]; it reaches a

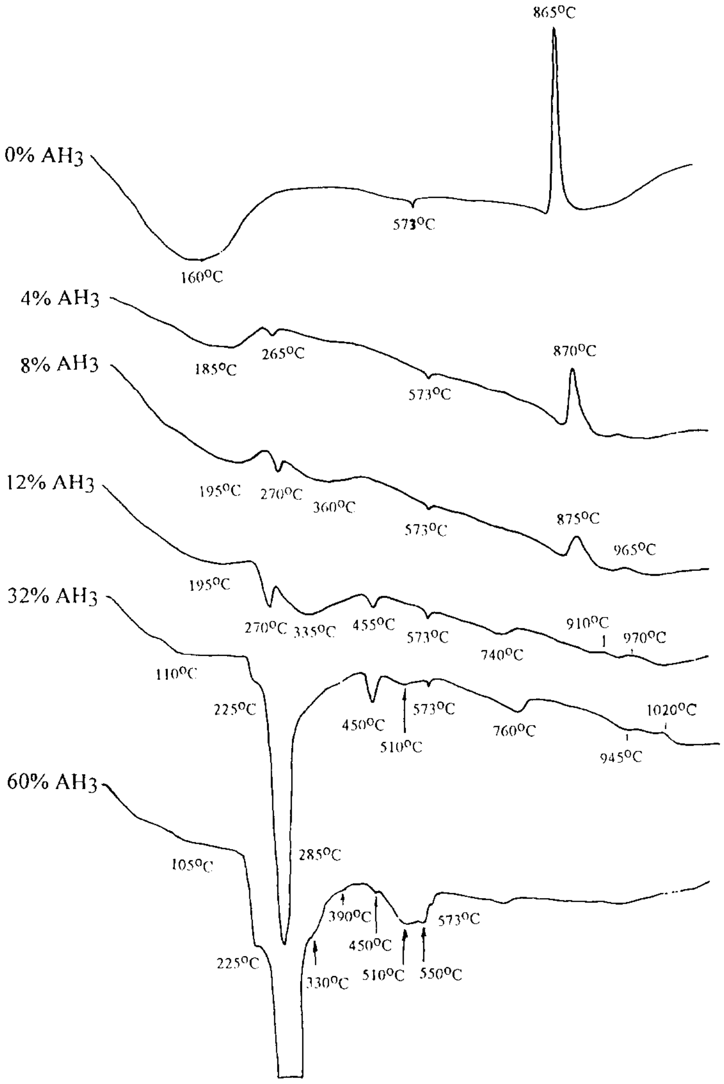

Fig. 1. Selected DTA curves of autoclaved cement–quartz mortars with various gibbsite additions.

maximum at 8% gibbsite addition, and has diminished considerably in size at 20% addition.

The peak heights, when plotted against gibbsite addition (Fig. 2), clearly show the initial small amount of unreacted gibbsite. After 8% gibbsite addition, there is an almost linear increase in unreacted gibbsite except for the 36% addition, suggesting a predominance of C_3AH_6 formation in preference to the hydrogarnet [C_3ASH_4]. Above 44% gibbsite addition, the size of the unreacted gibbsite endotherm was excessive.

X-ray diffraction analysis was conducted on some of these specimens in

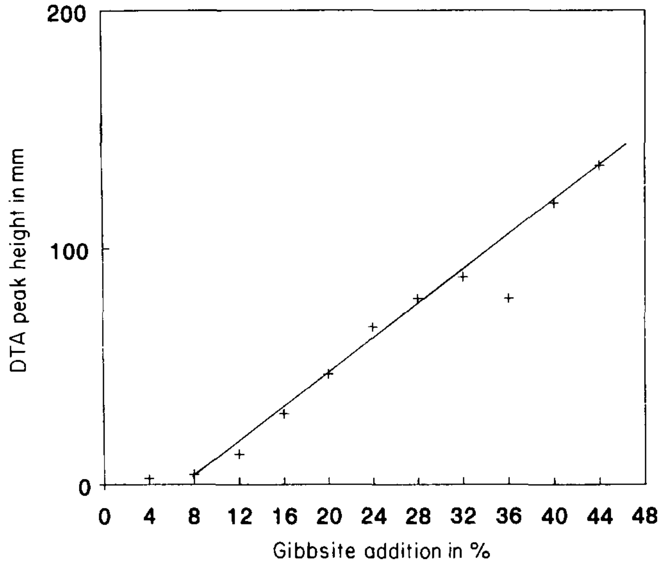

Fig. 2. Heights of the gibbsite dehydroxylation endothermic peak at 265–285°C as a function of gibbsite addition.

order to verify the DTA results. Unreacted quartz was detected in all specimens while unreacted gibbsite was detected only at 36% and 52% gibbsite additions. Although unreacted gibbsite is expected to be present in the sample with 12% gibbsite as found by DTA, the XRD analysis failed to detect it in this specimen due to its low abundance. No change in the XRD patterns was observed in specimens with low additions of AH_3, in keeping with the observations of Kalousek [3].

CONCLUSION

During autoclaving, new phases can form readily through chemical reactions and it is important to consider their effect, especially the role of the minor phases, on the overall properties of the cements. In this study, DTA has proved to be a highly successful technique in providing important information concerning the phase transformations occurring at various levels of gibbsite addition in the cement–quartz autoclave reaction. For instance, with a small addition (2%) of gibbsite, the initial formation of hydrogarnet at the expense of CSH(I) could be detected by DTA. Hydrogarnet is important in inhibiting the carbonation reaction.

REFERENCES

1 S.M. Bushnell-Watson and J.H. Sharp, Thermochim. Acta, 93 (1985) 613–616.
2 Z. Sauman, O. Hoffman and I. Kocuvan, Silicaty, 25(4) (1981) 297–307.
3 G.L. Kalousek, J. Am. Ceram. Soc., 40 (1957) 74.

4 T. Mitsuda, K. Sasaki and H. Ishida, J. Am. Ceram. Soc., 75(7) (1992) 1858–1863.
5 N.B. Milestone, T. Sugama and L.E. Kukacka, Ceram. Concr. Res., 16(6) (1986) 941–950.
6 B.-Z. Sun, G.-C. Li and C. Jia, Guisuanyn Xuebao (J. Chinese Silicate Society), 11(1) (1983) 77–84.
7 H.F.W. Taylor, Chemistry of Cement, Proc. 4th Int. Symp. Chem. Cements, Washington, 1962, Natl. Bur. Stand. (U.S.), Monogr. No. 43, Vol. 1, U.S. Dept. Commerce, 1962, pp. 167–190.
8 G.E. Bessey, in H.F.W. Taylor (Ed.), The Chemistry of Cements, Vol. 2, Academic Press New York, 1964, p. 109.
9 S.K. Mehta, A. Malcotra and M. Murat, Thermochim. Acta, 205 (1992) 191–203.
10 R.F. Feldman and V.S. Ramanchandran, J. Am. Ceram. Soc., 49 (1966) 268.