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Note

Use of DTA to determine the effect of mineralizers on the cement–quartz hydrothermal reactions. Part 2. Clay addition

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Abstract

The effect of adding up to 40% by weight of kaolinite and metakaolinite to cement–quartz mortars hydrothermally cured (autoclaved) at 175°C was investigated by DTA. It is evident that aluminium substitution in the CSH-I lattice takes place with the clay additions in a manner similar to that observed for gibbsite addition, as reported in the previous paper (Part 1, Thermochim. Acta, 224 (1993) 241). Comparison between kaolinite and metakaolinite additions shows kaolinite to be the less reactive phase in these autoclaved cement–quartz mortars.

Keywords: Autoclaving; CSH; DTA; Hydrogarnet; Kaolinite; Metakaolinite; XRD

1. Introduction

The pozzolanic behaviour of burnt clays has been known from the Roman era [1], and for over 150 years burnt clay pozzolanic cements have been manufactured commercially [2]. Burnt kaolinite and hydrated lime are known to form gehlenite

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[1] Cement chemistry nomenclature: C, CaO; S, SiO_2; A, Al_2O_3; H, H_2O.

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hydrate [C_2ASH_8]^1 at 20°C and a hydrated calcium silicate of the tobermorite group with a variable CaO/SiO_2 ratio. With increasing temperature, the gehlenite hydrate becomes unstable until, at a temperature of 50°C, the hydrated Al_2O_3-containing phase is a hydrogarnet of approximate composition $C_3AS_{0.3}H_{5.3}$ [3].

Although kaolinite belongs to the triclinic system, its most common habit is fine, flaky, pseudohexagonal crystals usually observable only under very high magnification, such as the electron microscope. It is well known that the rate of tobermorite formation in autoclaved cement–quartz mortars is accelerated by the addition of reactive aluminous materials [4]. In this respect, kaolinite, which is cheap and highly reactive, provides a suitable source.

The ideal formula for kaolinite is $Al_4Si_4O_{10}(OH)_8$, consisting of approximately 46.5 wt% silica, 39.5 wt% alumina and 14 wt% water. The bound water is present as hydroxyl groups and, according to DTA and TGA studies [5], is lost between 400 and 525°C (dehydroxylation), forming metakaolinite [6]. At ≈1000°C, this metakaolinite converts to mullite the cristobalite [7]. This is demonstrated in Fig. 1.

2. Experimental

Metakaolinite is usually manufactured by heating kaolinite to a temperature of ≈700°C for at least one hour [8] to maximise its pozzolanic activity [9]. Metakaolinite is finer grained than kaolinite and its addition to cement mortars inhibits the alkali–aggregate reaction and reduces alkali attack of glass fibre reinforced cement [8].

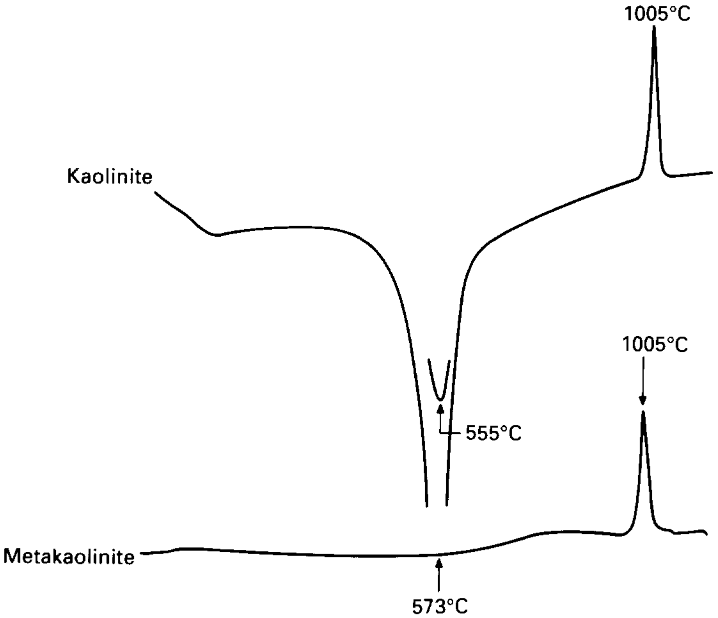

Fig. 1. DTA of kaolinite and metakaolinite.

In this work it was necessary to reduce the pozzolanic activity of the metakaolinite at room temperature to ensure that the reaction takes place during the autoclave heating cycle and not at room temperature. Thus, the kaolinite was heated at 900°C to produce a metakaolinite with reduced pozzolanic activity.

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, Australia.
Kaolinite:	Commercial Minerals (NSW).
Metakaolinite:	manufactured from the kaolinite by heating it at 900°C for 6 h, then cooling at ≈ 20°C min^{-1} to 600°C and then air-cooling in a desiccator.

The specimen preparation and curing conditions were similar to those described in Part 1 [10]. Kaolinite and metakaolinite additions of 0, 4, 10, 20 and 40% were made. A constant water/(cement + kaolinite or metakaolinite) ratio of 0.36 was used for the preparation for autoclaving. Equal weights of cement and quartz (total 200–400 g) were weighed into a 500 g glass jar and thoroughly mixed. Specimen preparation consisted of this premixed blend plus various amounts of kaolinite or metakaolinite to a total of 25 g. To this was added 9 ml of water, with thorough mixing, prior to transferring to a 50 mm × 25 mm square histology mould.

The moulds were exposed to the 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. Each sample for DTA was taken from the core of the specimens and finely ground before thermal analysis. Thermal analyses were performed on a Rigaku 8008HT thermal analyser with a micro-DTA head using a heating rate of 10°C min^{-1} under dry nitrogen with a flow rate of 0.2 ml min^{-1}. Sample size was ≈ 50 mg. A sintered 1 : 1 Al_2O_3/kaolinite mixture was used as the reference material. X-ray diffraction (XRD) analysis of the sample was carried out from 2 to 55° 2θ at 1° 2θ per min using cobalt $K\alpha_1$ radiation.

3. Results and discussion

Fig. 1 shows that both kaolinite and metakaolinite exhibit an exotherm indicating phase transformation to mullite. However, less mullite is produced from the metakaolinite than from the kaolinite when comparing the heights of the exotherms at 1005°C. The metakaolinite thermal curve also shows a slight contamination by quartz, indicated by the small, sharp endotherm at 537°C. This contamination is estimated to be ≈ 1%. As expected, the main endotherm associated with dehydroxylation in kaolinite at 550°C is absent in metakaolinite.

Fig. 2 compares the addition of 4% of kaolinite, and of its aluminosilicate equivalent 3.64% of metakaolinite, which has been corrected for its loss of hydroxyl-

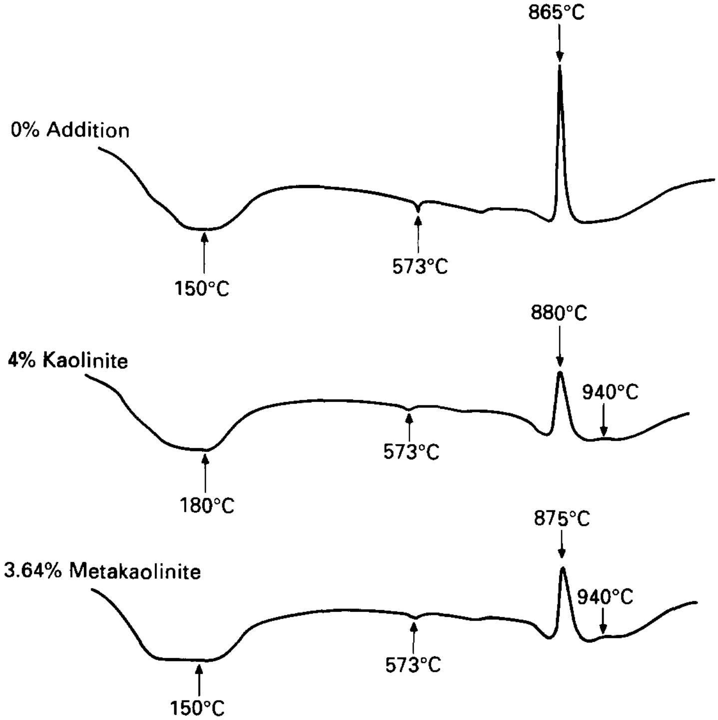

Fig. 2. Direct comparison of kaolinite and metakaolinite. Cement/quartz ratio 50/50.

water. The DTA peaks in Fig. 2 are ascribed to [10] dehydration of the calcium silicate hydrate 150–225°C, crystalline inversion due to unreacted quartz at 573°C, wollastonite formation at 865–915°C from calcium silicate hydrate, and formation of anorthite from hydrogarnet at 940–985°C. The kaolinite and metakaolinite additions gave very similar thermal curves. When compared with the 0% (control) thermal curve they exhibit

(i) an increase in the aluminium content of the calcium silicate hydrate, as indicated by the reduction in the height of the 865–880°C exotherm [11]. The temperature of this exotherm shifts by up to 15°C.

(ii) the presence of hydrogarnet, as indicated by the existence of a very small exotherm at 940°C [10], and

(iii) a smaller content of unreacted quartz, as shown by the variation in size of the endotherm at 573°C.

Figs. 3 and 4 illustrate the effects of the addition of metakaolinite and kaolinite respectively where no correction has been made for the loss of hydroxyl water in the metakaolinite. Thus, 20% of metakaolinite corresponds to an aluminosilicate addition of 22% of kaolinite. The dehydroxylation endotherm at ≈170°C due to calcium silicate hydrate decreases in area. For the exotherm at 865°C, the gradual

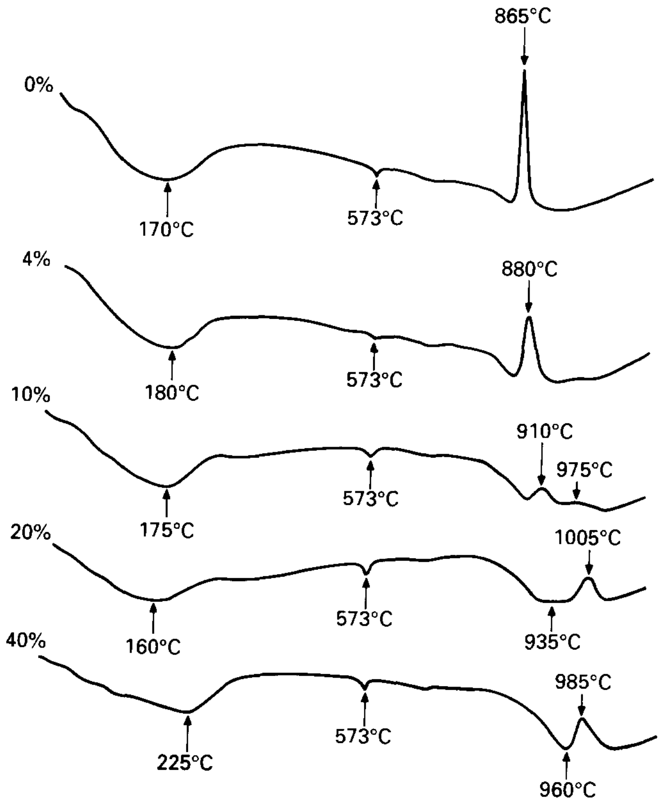

Fig. 3. Metakaolinite addition. Cement/quartz ratio 50/50.

decrease in size with a corresponding increase in temperature indicates that alumina has been incorporated into the calcium silicate hydrate lattice [11]. Concurrently, the second exotherm at ≈940°C (due to hydrogarnet formation) increases in height and in peak temperature. Judging from the relative heights of this exotherm, the addition of kaolinite appears to accelerate hydrogarnet formation when compared with metakaolinite addition.

The dehydroxylation endotherm at ≈500°C in Fig. 4 indicates the presence of unreacted kaolinite for additions of 20% of kaolinite to 50/50 cement–quartz mortars. The area of this endotherm increases with increasing addition of kaolinite. The presence of the mullite transformation exotherm above 1000°C in samples with 20% and greater addition of kaolinite confirms the existence of unreacted kaolinite. The absence of this mullinite transformation exotherm in Fig. 3 suggests that, up to an addition of 40%, metakaolinite has fully reacted, unlike kaolinite, where the large excess of unreacted kaolinite has diminished the other peaks by dilution.

Results obtained by XRD confirmed the above discussion and, as in Part 1 [10], DTA has proved to be the more sensitive technique.

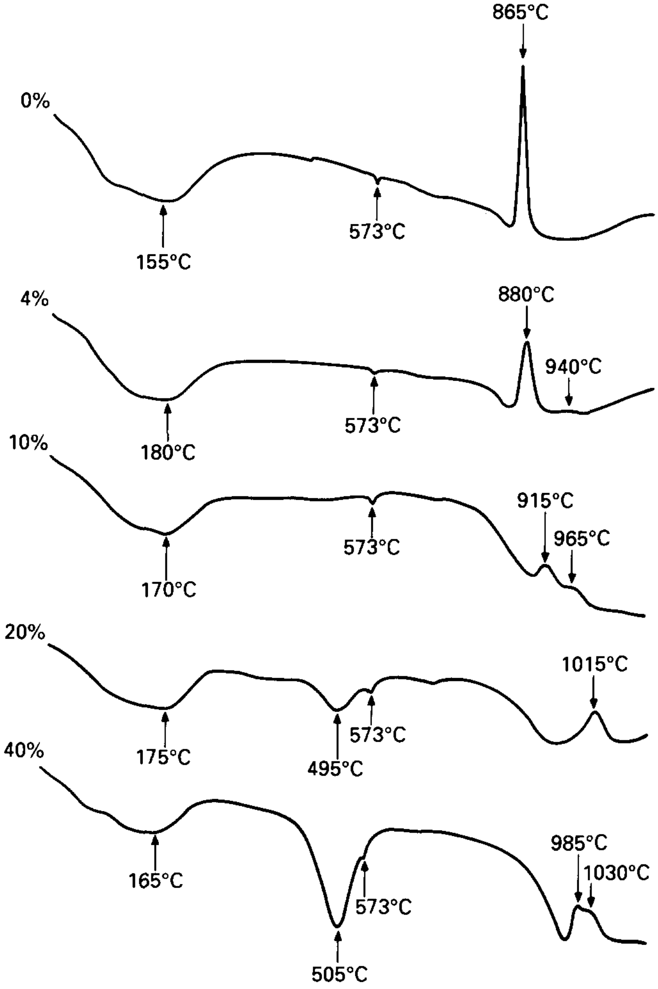

Fig. 4. Kaolinite addition. Cement/quartz ratio 50/50.

4. Conclusions

This study had led to the following conclusions.

(1) Similar to the results reported for gibbsite [10], the increasing addition of metakaolinite and kaolinite caused increasing aluminium substitution into the calcium silicate hydrate lattice [11].

(2) At the above 20% addition, some unreacted kaolinite remains.

(3) The addition of kaolinite or metakaolinite does not affect the cement–quartz reaction, as indicated by the area of the 573°C endotherm remaining constant.

(4) Metakaolinite has proved to be more reactive than kaolinite in autoclaved cement–quartz reactions.

References

[1] W.H. Taylor, Cement Technology, 4th edn., McGraw-Hill, 1977, Chap. 17, pp. 327–333.
[2] F.M. Lea, The Chemistry of Cement and Concrete, 3rd edn., Edward Arnold, 1970, pp. 419–421.
[3] R. Turruziani, Aspects of the chemistry of pozzolanas, in H.F.W. Taylor (Ed.), Chemistry of Cements, Vol. I, Academic Press, London, 1964, Chap. 14, pp. 75–77.
[4] H.F.W. Taylor, Chemistry of Cement, Proc. 4th. Int. Symp. Chem. Cements, Washington, Natl. Bur. Std. (U.S.) Monogr., No. 43, U.S. Dept. Commerce, 1962, pp. 167–190.
[5] A.K. Chakraborty, J. Am. Ceram. Soc., 75(7) (1992) 2013.
[6] M.H. Battey, Mineralogy for Students, 2nd edn., Longmans, London, 1982, p. 270.
[7] R.E. Grim, Clay Mineralogy, McGraw-Hill, 1968, pp. 285–297.
[8] R. Kondo and S. Ohsawa, J. Am. Ceram. Soc., 62(9–10) (1979) 447.
[9] J. Ambroise, M. Murat and J. Pera, Cem. Concr. Res., 15(1) (1981) 83.
[10] E.R. Cantrill, M.G. Stevens, A. Ray and L. Aldridge, Thermochim. Acta, 224 (1993) 241.
[11] G.L. Kalousek, J. Am. Ceram. Soc., 40 (1957) 74.