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THERMAL CHARACTERISATION OF AUTOCLAVED CEMENT MADE WITH ALUMINA-SILICA RICH INDUSTRIAL WASTE

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The hydration products of hydrothermally cured OPC-quartz blends incorporating clay-brick waste were characterised using simultaneous DTA-TG, XRD and SEM. The exotherm above 800°C on the DTA curve, due to the formation of β-wollastonite (β-CS) was related to the compressive strength. The area and/or height of the exotherm increased with compressive strength and was due primarily to the presence of calcium silicate hydrate phases including 1.1 nm tobermorite. Supporting evidence is provided by XRD and SEM.

Keywords: *autoclaving, clay-brick waste, compressive strength, thermal analysis, tobermorite*

Introduction

The trend towards the use of renewable resource materials in the manufacture of building products is driven by both economic factors and public awareness of environmental issues. Each year vast quantities of construction and demolition (C&D) waste are deposited in landfills globally. For example, according to the Environmental Protection Authority (EPA) of NSW, Australia, approximately 25% of C&D waste, equating to approximately 1 million tonnes, ended up in landfills in 1999 alone [1], and this situation can be avoided by making use of emerging technologies. Alumina-silica rich industrial waste in the form of fired clay-brick is generated in abundance on a global scale during production, transportation and construction procedures where large amounts are broken.

Previous research has shown that clay-brick, in a finely ground state, exhibits high pozzolanic activity under ambient conditions [2]. Hydrothermal curing or autoclaving, a process that affords rapid strength development by the use of saturated steam under pressure, enhances the chemical reactivity of pozzolanic materials [3]. Klimesch and Ray demonstrated that the formation of 1.1 nm tobermorite, the principal binding agent of calcium silicate based products, is enhanced by the addition of finely ground clay-brick to mixtures of ordinary Portland cement (OPC) and quartz sand [4–6].

Many studies have been reported on the compressive strength development of autoclaved calcium silicate materials containing tobermorite as the main binder. Factors that are considered important in relation to compressive strength include the amount of crystalline to amorphous binding material at a given porosity, the particle size distribution and amount of unreacted starting material and the crystal habit of tobermorite [7–13]. This article presents preliminary results from simultaneous DTA-TG, X-ray powder diffraction and scanning electron microscopy in relation to compressive strength development.

Experimental

The feasibility of utilizing clay-brick waste for the manufacture of cement-based building products was the subject of previous research examining the combined influence of factors on the strength development using a factorial experimental design [14]. The factors chosen were: autoclaving time, autoclaving temperature and cement: quartz replacement level (additive amount) with the response variable being compressive strength. A more detailed account of the factorial experimental design approach is given elsewhere [15]. Table 2 in the results and discussion section provides a summary.

Materials

- Type A ordinary OPC produced by Australian Cement, Auburn, NSW, Australia with a Blaine fineness of 350 m^2 kg^{-1}. It contained SiO_2 20%, CaO 64.2%, Al_2O_3 4.5%, Fe_2O_3 3.7% and SO_3 3.5%.

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- Ground quartz sand (Quartz) supplied by Unimin Australia Limited, Sydney, Australia with a mean particle diameter of 22 micron and a Blaine surface area of 360 m^2 kg^{-1}. It contained SiO_2 98.9%, Al_2O_3 0.6%, Fe_2O_3 0.1% and TiO_2 0.06%.
- Clay-brick waste supplied by a major clay-brick manufacturer in Sydney, Australia, was crushed to less than 2.38 mm followed by dry ball milling to achieve a particle size distribution comparable to that of the quartz used. The major crystalline phases of the clay-brick, as determined by X-ray powder diffraction (XRD), were: quartz, mullite, hematite, with minor amounts of cristobalite and rutile. The major oxides as determined by X-ray fluorescence (XRF) are given in Table 1.

Table 1 Major oxide composition of brick fines from XRF analysis

Major oxides	Mass%
SiO_2	69.71
Al_2O_3	18.64
Fe_2O_3	7.48
K_2O	1.88
MgO	0.95
TiO_2	0.84
Na_2O	0.44
CaO	0.21
LOI	0.08

LOI: loss on ignition at 1050°C for 2 h

Sample preparation

OPC–quartz–clay-brick blends were prepared using a water-to-total solids ratio (*w*/*s*) of 0.33 as this yielded similar workability for all the mixtures. A cement: quartz ratio comparable to commercially manufactured building products of 0.67 was used. Mechanical mixing of these blends was conducted in accordance with ASTM C305-99 [16]. Clay-brick was added at 4.3 and 8.6 mass% as cement:quartz replacement. Pastes were cast into stainless steel moulds and consolidated on a vibratory table, followed by precuring for 24 h in a moist cabinet. For each mix three 50 mm^3 cubes were cast. Demoulded cubes were autoclaved according to the following autoclave regime: 1.5 h ramping up to the required temperature, followed by 6 or 8 h of steam saturation and then ramping down to ambient temperature. Autoclaved specimens were then allowed to air dry for 48 h prior to mechanical testing. The bulk density of cubes was determined by mass and volume measurements. Compressive strength was measured according to ASTM C109-02 [17]. The specimens were loaded under compression until failure using a Tinius Olsen instrument. Average compressive strength data of all acceptable test specimens per mould are reported to the nearest 0.1 MPa. After mechanical testing samples were oven dried overnight at around 105°C followed by disc milling. Duplication of the experimental design as outlined in Table 2 was performed.

Methods

A TA Instruments SDT 2960 simultaneous DTA-TG analyzer was used to measure the mass change and temperature difference of samples with increasing temperature. The mass range of powdered samples was between 20–30 mg. Each sample was evenly packed into an open Pt–Rh crucible with 20 taps. Samples were analysed at a heating rate of 10°C min^{-1} under flowing air at 20 mL min^{-1} from 25 to 1000°C. DTA-TG curves were evaluated using the TA Instruments analysis software with two-point rotations carried out for all curves.

X-ray diffraction analysis was carried out using a Siemens D5000 X-ray powder diffractometer with symmetrical Bragg–Brentano geometry. An X-ray tube was used at a power of 40 mA and 40 kV to produce CuK_α radiation (λ=0.1540981 nm). Samples were mounted in plastic sample holders. The holder and sample were placed on the diffractometer and an

Table 2 Results for autoclaved cement blends using TA instruments DTA-TG data analysis software. Compressive strength results are the average values from duplicate runs

Sample	Autoclave time/h	Autoclave temperature/°C	Additive amount/%	Compressive strength/MPa	Exotherm peak maximum/°C
1	8	170	8.6	77.7	846
2	8	170	4.3	75.0	845
3	6	170	4.3	72.3	847
4	6	170	8.6	68.2	847
5	6	180	4.3	64.7	846
6	8	180	4.3	60.8	844
7	8	180	8.6	59.0	846
8	6	180	8.6	54.4	846

XRD pattern collected for 2θ values from 3.000 to 65.000°, at intervals of 0.020°. Step times of 6 s per interval were employed and the receiving-slit width was 0.2 mm. The ICDD-JCPDS Powder Diffraction File CD-ROM was used for qualitative phase identification. A fundamental parameters approach was used for X-ray line profile fitting in order to determine peak heights and areas [18].

Microstructural analysis of the cement samples was carried out on a Jeol 6300F field emission scanning electron microscope (FEGSEM) at an accelerating voltage of 30 kV. Samples were deposited on aluminum discs and placed under vacuum prior to carbon coating. Images were recorded on either a Mitsubishi video printer or captured digitally using Moran Scientific X-ray mapping software. Images that were collected digitally were acquired at 512 by 512 pixel resolution.

Results and discussion

Differential thermal (DTA) curves of autoclaved specimens are depicted in Fig. 1. The main observed endotherms (endo) and exotherms (exo) are ascribed to:

ca. 105 to 260°C (endo) not shown	presence of calcium silicate hydrates (C–S–Hs) including 1.1 nm tobermorite ($C_5S_6H_5$)
ca. 260 to 350°C (endo) not shown	presence of a member of the hydrogarnet series, $C_3AS_{3-x}H_{2x}$, x=0 to 3
ca. 573°C (endo)	crystalline inversion due to unreacted quartz (Q)
ca. 600 to 700°C (endo)	decarbonation of $CaCO_3$
ca. 800 to 900°C (exo)	crystallization of beta-wollastonite (β-CS) from C–S–Hs including ($C_5S_6H_5$) were present

The variations in the observed exotherm temperatures with compressive strength are given in Table 2 along with sample ID and experimental conditions. The exotherm temperatures of the autoclaved blends were within a very narrow range, suggesting that the binding material present was of a similar nature.

It is well known that the exotherm profile due to β-CS formation is affected by the nature of the precursor calcium silicate hydrate phases including: Ca/Si ratio, Al-content and presence of other foreign ions such a K^+ and Na^+ [19, 20].

The relationship between compressive strength *vs.* exotherm area and height is shown in Fig. 2. Purton [9] found that for autoclaved cement-bound specimens the area of the exotherm increased with the amount of binder in the original mix. Alexanderson [8] found a positive correlation between the exotherm peak height and the content of C–S–H(I) in the absence of supplementary addition of Al-containing materials. In contrast when Al-containing materials were used the peak height increased and was attributed to Al-tobermorite. It follows, that the observed increase in exotherm area and height can therefore be attributed to the development of increasing quantities of calcium silicate hydrate phases including 1.1 nm tobermorite.

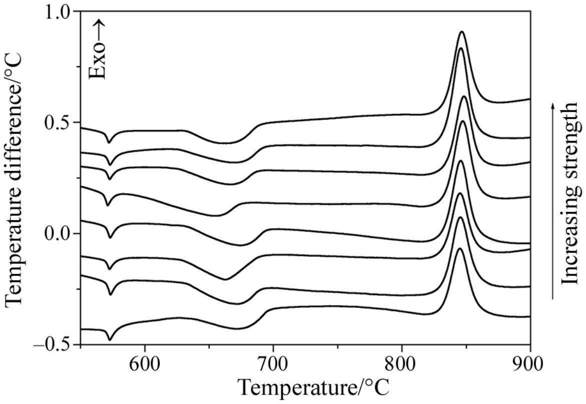

Fig. 1 Representative DTA curves for hydrothermally treated specimens containing clay-brick waste of increasing strength from bottom to top as Table 2

The relationship between the compressive strength as a function of bulk density is shown in Fig. 3. The data show increased compressive strength with increasing bulk density. Previous work showed that generally, there is a reverse relationship between bulk density and apparent porosity. It may be concluded, that increased compressive strength was a consequence of the filling up of available pore volume with the crystallization of hydration products, including tobermorite, which correlates well with the thermal data. We are currently conducting a more detailed study of microstructural attributes including the

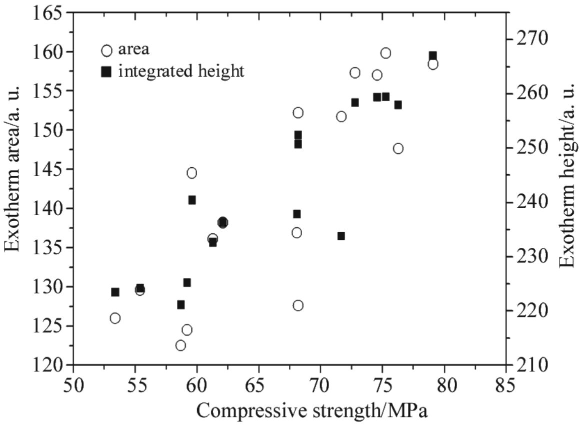

Fig. 2 Showing the correlation between compressive strength and the area and height of the exothermic peak on DTA curves with duplicates plotted; a. u. – arbitary units

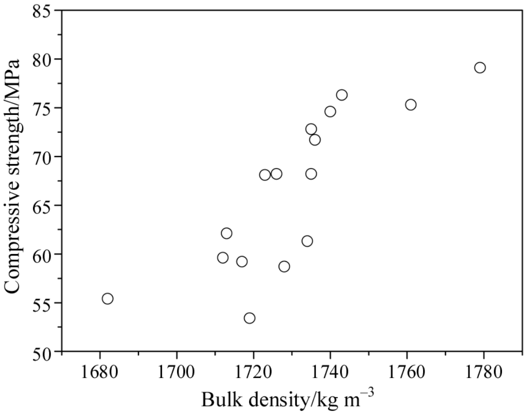

Fig. 3 Bulk density of autoclaved blends as a function of compressive strength for hydrothermally treated specimens containing clay-brick waste

nature of the pore structure and will report our findings in future publications.

As the exotherm temperature range for the specimens was within a very narrow range (Table 2) it may be concluded that the relationship between compressive strength and exotherm area/height is a function of the amount of binding material present.

Figure 4 shows the ratio of the relative XRD intensities of the 2.97/3.08 Å lines. With one exception, the data fall into two distinct groups for ratios of namely 0.35 to 0.40 and 0.45 to 0.50 ranges. According to Kalousek [21], this ratio of intensities can be used to differentiate between Taylor's C–S–H(I) (intensity ratio=0) and tobermorite (intensity ratio=0.7–0.8). It may be inferred that either the higher strength binder contains a more crystalline tobermorite, or alternatively, the ratio of crystalline to amorphous binding material has increased. Supporting evidence is provided by SEM.

For instance, from SEM observations the high strength specimen group, depicted in Figs 5 and 6, is predominantly of a lath-like morphology whereas the

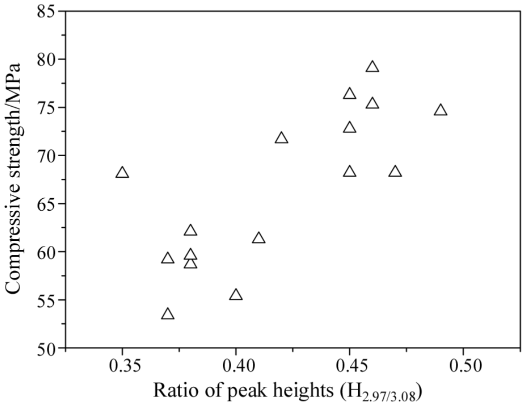

Fig. 4 Ratio of relative 2.97/3.08 Å X-ray line intensities of the binder for hydrothermally treated specimens containing clay-brick waste as a function of compressive strength

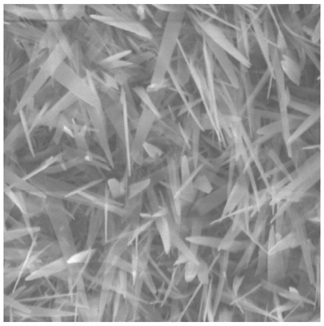

Fig. 5 Tobermorite in sample 1 with compressive strength of 77.7 MPa. Field of view (18.9×18.9 μm); magnification ×5000

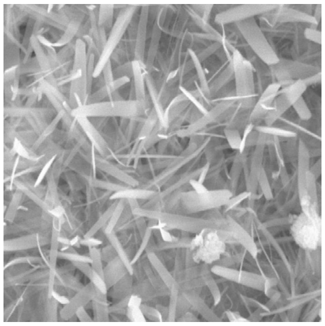

Fig. 6 Tobermorite in sample 2 with compressive strength of 75.0 MPa. Field of view (18.9×18.9 μm); magnification ×5000

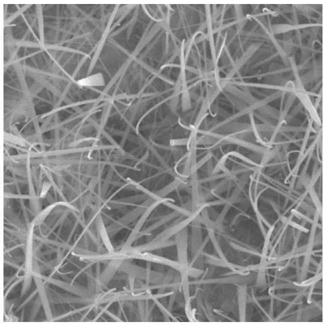

Fig. 7 Tobermorite in sample 7 with compressive strength of 59.0 MPa. Field of view (18.9×18.9 μm); magnification ×5000

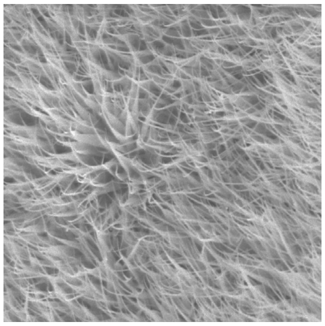

Fig. 8 Tobermorite in sample 8 with compressive strength of 54.4 MPa. Field of view (18.9×18.9 μm); magnification ×5000

low strength specimens (Figs 7 and 8) are more needle-like. It has been reported, that the morphology change, plate through lath-like to needle-like, is associated with a decrease in tobermorite crystallinity [12].

It is worth noting that the autoclaving temperature (Table 2) appears to play a significant role in the development of the particular morphologies observed. We are currently undertaking further investigations into the effect of temperature in relation to strength development.

Conclusions

From the data presented in this study we conclude:

- DTA-TG is a very useful technique in the study of hydrothermally cured $CaO–SiO_2–H_2O$ and $CaO–Al_2O_3–SiO_2–H_2O$ systems.
- Compressive strength is related to a combination of the quantity of binding material and crystal habit.
- In the system studied the exotherm peak above 800°C was a good indicator of the quantity of calcium silicate hydrate phases within OPC–quartz blends incorporating clay-brick waste. Compressive strengths were proportional to the exotherm area and height.
- From the relative XRD intensities of the 2.97/3.08 Å lines, it may be inferred that either the higher strength binder contains a more crystalline tobermorite, or alternatively the ratio of crystalline to amorphous binding material has increased. Supporting evidence was provided by SEM.
- A lower autoclaving temperature when using clay-brick waste was found to be beneficial for the formation of crystalline lathe-type tobermorite producing higher compressive strengths when compared to the higher autoclaving temperature.

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