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EFFECT OF AUTOCLAVING TEMPERATURE ON CALCIUM SILICATE-BASED BUILDING PRODUCTS CONTAINING CLAY- BRICK WASTE

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The utilisation of fired clay-brick waste is of interest in the manufacture of building products due to both socio-economic and technological reasons. Autoclaving is an established process for manufacturing calcium silicate-based building products that affords rapid strength development. Clay-brick waste represents a source of alternative silica, which is more reactive than conventionally used silica and also contains alumina. This paper presents data on the effect of lowering the autoclaving temperature from commonly practised 180 to 170°C on OPC-quartz blends containing clay-brick fines as direct replacement of quartz at 4.3, 8.6 and 12.9 mass percentages. The hydration products of autoclaved OPC-quartz blends with clay-brick fines were characterised using simultaneous DTA-TG in combination with other methods.

Keywords: *autoclaving, clay-brick waste, Portland cement, thermal analysis, tobermorite*

Introduction

Each year vast amounts of clay-brick waste are generated globally during production, transportation and construction procedures. The development of new technologies for the utilisation of this waste material, normally destined for landfill, will help avoid a growing cost in environmental damage caused each year. The construction industry has shown considerable interest in the utilisation of this solid waste, which is rich in Al_2O_3 and SiO_2. Fired clay-brick, in a finely ground state has been shown to exhibit high pozzolanic activity under ambient conditions [1]. In other words, it hardens in water when mixed with calcium hydroxide or with materials that release Ca^{2+} ions, such as Portland cement. It is well known, that the chemical reactivity of pozzolanic materials, and thus their effectiveness, is enhanced by temperature, and in particular, by autoclaving [2]. Autoclaving refers to curing in saturated steam under pressure typically at 180°C for several hours using mixtures of cement (OPC) and/or lime (30 to 80 mass%), finely ground quartz (70 to 20 mass%) and other additives (1 to 20 mass%). The process affords the manufacture of cement-based construction materials that have the principal advantage of permanent high early strength equivalent to that of 28 days ambient cured products. Industrial autoclaved cement-based building products are usually made with a cement: quartz ratio of about 40:60. Previous research conducted by this research group has shown that the formation of 1.1 nm tobermorite is enhanced by the addition of finely ground clay-brick waste to blends of OPC and quartz sand [3, 4]. Tobermorite, regarded amongst the most important of the hydrous calcium silicate phases, serves as the principal binder and provides the matrix strength associated with autoclaved cementitious building products. Thermal analysis has been employed extensively in the study of autoclaved cement-based systems in evaluating the nature of hydration products formed. Utilising DTA-TG the present work investigates the effect of a reduced autoclave temperature to assess the nature of clay-brick's hydrothermal reactivity.

Experimental

Materials

Raw materials

The following raw materials were used:

- Goliath cement (OPC) containing SiO_2 20%, CaO 64.2%, Al_2O_3 4.5%, Fe_2O_3, 3.7% and SO_3 3.5% and having a Blaine fineness of 350 $m^2\ kg^{-1}$ was supplied by Australian Cement, Auburn, NSW, Australia
- Ground quartz sand (Quartz) containing SiO_2 98.9%, Al_2O_3 0.6%, Fe_2O_3 0.1% and TiO_2 0.06%, with a mean particle diameter of 22 micron and a

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Blaine surface area of 360 m^2 kg^{-1} was sourced from Unimin Australia Limited, Sydney, Australia.

- 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 oxides as determined by X-ray fluorescence (XRF) are given in Table 1. Qualitative phase identification of the clay-brick was determined using X-ray powder diffraction (XRD). The crystalline phases present were identified using ICDD-JCPDS Powder Diffraction patterns and are summarized in Table 2, in decreasing order of abundance.

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 of 40:60 was used, being comparable to those used by industry. Mechanical mixing of these blends was conducted in accordance to ASTM C305-99 [5] with minor modifications. Clay-brick was added at 4.3, 8.6, 12.9 mass% as direct quartz replacement. Table 3 contains the chemical composition of the blends studied. 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 50·50·50 mm cubes were cast. Demoulded cubes were autoclaved according to the following autoclave regime: 1.5 h ramping up to the maximum temperature, either 170 or 180°C, followed by 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 [6]. The specimens were loaded under compression until failure using a Tinius Olsen instrument. The average compressive strength of all acceptable specimens per mould, at the same test age, is 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 regime outlined above was conducted to ensure reproducibility of mechanical testing results.

Table 1 Major oxide composition of clay-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

Table 2 Crystalline phases present in clay-brick fines in decreasing order of abundance

Crystalline phases	Composition
Quartz	SiO_2
Mullite	$3Al_2O_3·2SiO_2$
Hematite	Fe_2O_3
Cristobalite	SiO_2
Rutile	TiO_2

Instrumentation

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 20–25 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. The second derivative differential thermal curves were used for peak identification and peak temperature determinations. The amount of acid insoluble residue (AIR) was determined by a modified filtration method and provided a measure of the total unreacted material. The res-

Table 3 Chemical composition of pastes studied

Clay-brick mass/%	Cement:silica ratio	Atom ratio Ca/Si	Atom ratio Ca/(Al+Si)	Atom ratio Al/(Al+Si)	Atom ratio Al/Si
0.0	0.67	0.41	0.39	0.036	0.04
4.3	0.72	0.42	0.40	0.050	0.05
8.6	0.78	0.43	0.40	0.063	0.07
12.9	0.85	0.43	0.40	0.077	0.08

idues from triplicate AIR analyses were combined and the chemical composition determined by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP) by Genalysis Laboratory Services Pty Ltd., Western Australia. Peroxide fusion and multi-acid attack including hydrofluoric, nitric, perchloric and hydrochloric acids were used for the digestion of the residue.

Results and discussion

Compressive strength

The compressive strength results are given in Fig. 1.

At the outset the 170°C blend exhibits superior compressive strength in comparison to the 180°C blend. With the addition of clay-brick fines, a crossover, in relation to compressive strength occurs with the addition of the maximum silica replacement level used, namely 12.9 mass percent. No observable trends were noted between compressive strength and bulk density.

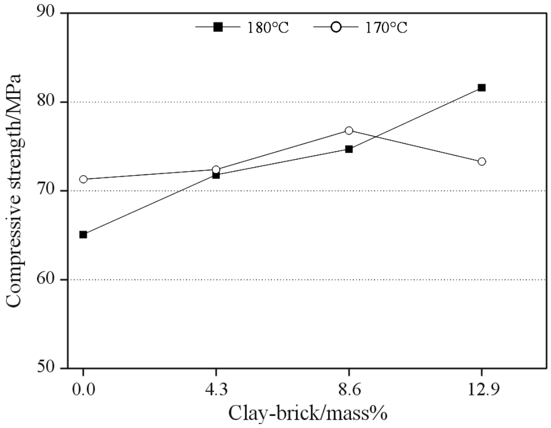

Fig. 1 Average compressive strength values for autoclaved blends

Thermal analysis

Differential thermal (DTA) curves of autoclaved specimens are depicted in Figs 2 and 3. The main observed endotherms (endo) and exotherms (exo) are ascribed to:

- ca. 105 to 260°C (endo): presence of calcium silicate hydrates (C–S–Hs) including 1.1 nm tobermorite ($C_5S_6H_5$) were present;
- ca. 573°C (endo): crystalline inversion due to unreacted quartz (*Q*);
- ca. 620 to 700°C (endo): decarbonation of $CaCO_3$;
- ca. 820 to 880°C (exo): crystallization of β-wollastonite (β-CS) from C–S–Hs including ($C_5S_6H_5$) were present.

Hara and Inoue [7] reported that the addition of alumina to mixture of CaO and fumed SiO_2 broaden and shift the exothermic peaks at ~800 to 900°C, attributed to beta-wollastonite (β-CS), to higher temperatures and increase their abundance. Similarly Kalousek [8] observed that increasing the Al content in tobermorite raised the β-CS formation temperature and made the exotherm flatter and broader. The presence of Al accelerates the rate of tobermorite formation with the Al substituting for Si in the tetrahedral sites of the tobermorite structure (Al-tobermorite) [2, 8, 9]. From a durability viewpoint this Al-tobermorite is regarded as more beneficial than Al-free tobermorite [10].

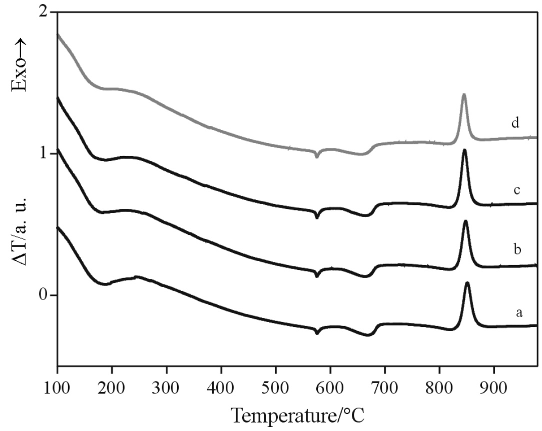

Fig. 2 DTA curves of 180°C autoclaved blends respectively from bottom to top: a – 12.9; b – 8.6; c – 4.3 mass% clay-brick and the d – control

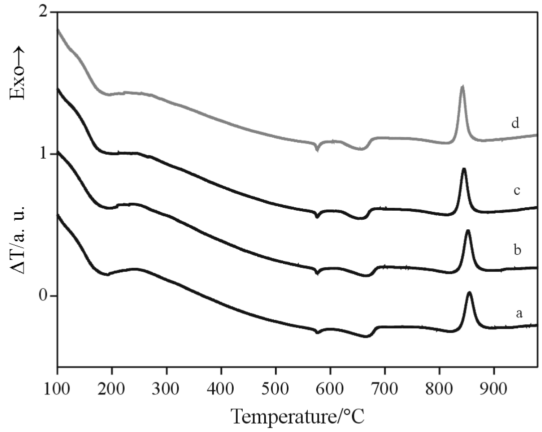

Fig. 3 DTA curves of 170°C autoclaved blends respectively from bottom to top: a – 12.9; b – 8.6; c – 4.3 mass% clay-brick and the d – control

It is clear from Fig. 4 that an increasing amount of Al was incorporated into the tobermorite crystal lattice with clay-brick fine addition up to 12.9 mass percent. The increase in the β-CS formation temperature correlates well with the increase in clay-brick mass addition and hence total Al_2O_3 content in the initial raw mix. Overall the exotherm profiles suggest greater alumina incorporation in samples autoclaved

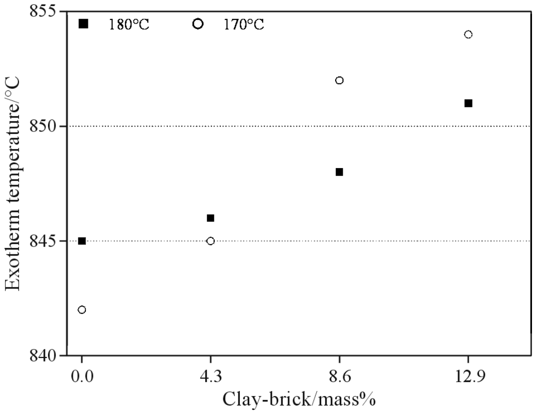

Fig. 4 Variation in the β-CS crystallization peak temperature *vs.* clay-brick addition

at 170°C, with the exception of the sample containing no clay-brick.

AIR analysis

Results of the analysis of the bulk and combined AIR compositions, for samples autoclaved to 170 and 180°C, are shown in Figs 5–7.

The following equation was employed to determine the combined CaO in the binding material:

$$\text{Combined CaO}=\text{bulk}-[1.27\cdot L_{\text{dc}}] \qquad (1)$$

where L_{dc} is the mass loss due to decarbonation between ~ 620 to 980°C.

The correction factor of 1.27 assumes that the carbonate was formed by carbon dioxide reacting with calcium hydroxide (CH) present during hydration [11].

The availability of CaO with the addition of clay-brick fines remained constant due to direct quartz replacement, whilst Al_2O_3 increased and SiO_2 decreased. Figure 5 shows that the reduced amount of SiO_2 did not result in less CaO being consumed in the formation of hydration products; CaO combined equally well at both 170 and 180°C, and with increasing clay-brick quantities.

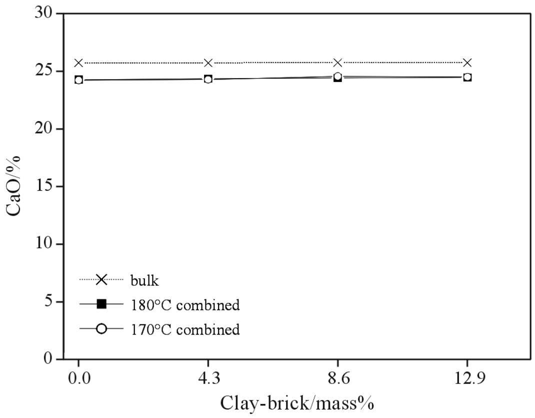

Fig. 5 Composition of bulk CaO and combined AIR of autoclaved blends with clay-brick addition

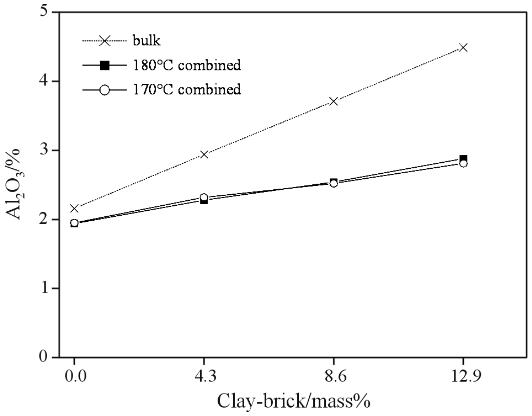

Fig. 6 Composition of bulk Al_2O_3 and combined AIR of autoclaved blends with clay-brick addition

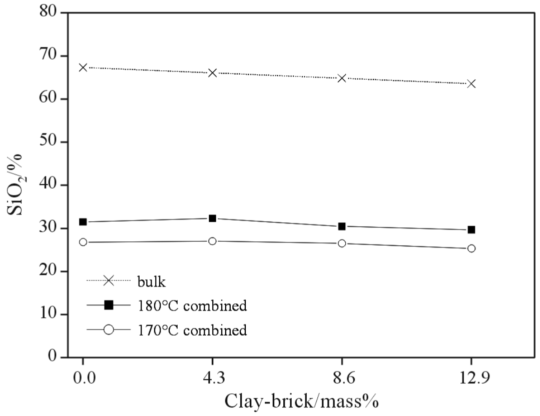

Fig. 7 Composition of bulk SiO_2 and combined AIR of autoclaved blends with clay-brick addition

The results for combined Al_2O_3 (Fig. 6) show that as the bulk Al_2O_3 increased the combined Al_2O_3 also increased. This indicates that the Al_2O_3 from the clay-brick fines was reactive at both temperatures, suggesting Al ions were progressively incorporated in the structure of those phases formed, namely hydrogarnet and Al-substituted tobermorite, the presence of which was confirmed by XRD. The finding correlates well with thermal analysis.

Most notable of Fig. 7 is the distinct difference on the level of combined SiO_2 between 170 and 180°C. The samples autoclaved at 180°C contain more combined silica than those at 170°C. It should be noted that the source of this is due to the temperature and not clay-brick addition as its occurrence is noted even without the addition of clay-brick. The lower curing temperature appeared to have reduced the rate of silica consumption.

The calculated Ca/Si atom ratio of the binding material shows an initial reduction followed by a continual increase suggesting the ratio of crystalline/amorphous content of the binder decreased over-

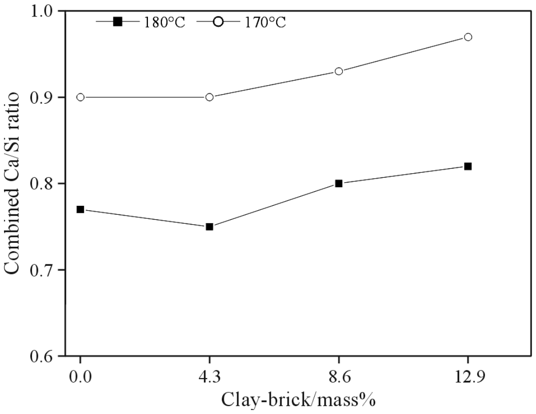

Fig. 8 Combined Ca/Si atom ratio of the binding material

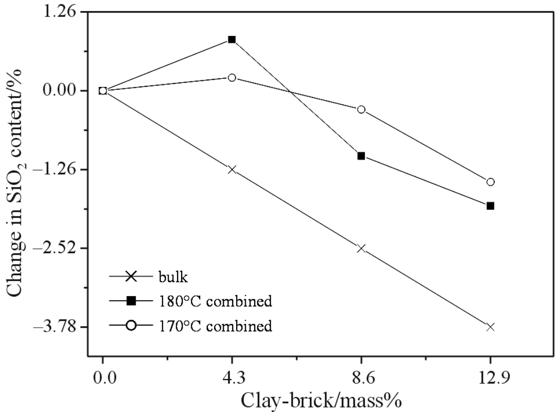

Fig. 9 Change in SiO_2 content with clay-brick addition

all with the addition of clay-brick (Fig. 8). In other words, a transformation of SiO_2 rich phases into low SiO_2 phases occurred. Additionally as a consequence of the reduced silica reactivity, C–S–H, of a high Ca/Si ratio, may have prevailed longer at 170°C and as such the crystalline/amorphous content is less. It is well known that the amount of crystalline to amorphous binding material is considered significant amongst other factors important to compressive strength [12–19].

With the addition of clay-brick fines a minor increase in combined SiO_2 is observed followed by a steady decrease. Both Figs 8 and 9 show a transformation of SiO_2 rich phases into low SiO_2 phases as occurring. The SiO_2 in the clay-brick is consequently more reactive in comparison to that SiO_2/ground quartz sand which it replaces.

Conclusions

From the finding presented in this study we can conclude the following:

- DTA-TG revealed that clay-brick is an excellent source of reactive material for use in hydrothermally cured $CaO–SiO_2–H_2O$ and $CaO–Al_2O_3–SiO_2–H_2O$ systems.
- The use of clay-brick in combination with OPC-quartz enhanced the formation of calcium silicate hydrates including tobermorite resulting in improved compressive strength.
- Mullite, the aluminosilicate phase contained in clay-brick, is reactive under hydrothermal conditions with the release of Al_2O_3 and SiO_2 occurring at or before 170°C.
- A lower autoclaving temperature with the use of clay-brick fines for autoclaved materials is likely with little adverse effect in mechanical properties. Further investigation is required with regard to phase formation at lower temperatures with regard to durability.

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