# technical paper

# Comparative Study of Finely Ground Fired Clay Brick and Kaolin Based Fillers in Autoclaved Calcium Silicate Based Building Products

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**ABSTRACT:**    The process of hydrothermal curing or autoclaving is particularly well suited to the utilisation of industrial by-products in the production of construction materials as it renders some of these waste materials highly reactive. Research findings have demonstrated that when used in combination with Portland cement (OPC) in the industrially important $CaO-Al_2O_3-SiO_2-H_2O$ system, finely ground fired clay brick masonry, an aluminosilica rich waste, is suitable for the production of autoclaved construction materials. The use of kaolin clay as a filler in the production of these autoclaved calcium silicate based building products is well established. This paper presents a comparative study of finely ground clay brick industrial waste and kaolin clay used in combination with OPC under autoclaved conditions. The observed variations in compressive strength are discussed in the context of the presence of critical phases, which were characterised by microstructural and thermal analytical methods.

## 1. INTRODUCTION

The process of autoclaving refers to curing in a stream-pressurised vessel at temperatures typically around 180 °C for several hours (Taylor, 1997). The principal advantage of autoclaving is the manufacture of cement-based materials that have permanent high early strength equivalent to that of 28 day ambient cured materials (Purton 1970). Autoclave cured cementitious materials are typically made using mixtures of cement (OPC) and/or lime (35 to 50 wt %), ground sand (40 to 65 wt %) and other minor additives (0 to 40 wt %) including fillers, water reducing agents, fire retardants, etc. The use of aluminosilicate clay-based fillers is a common industry practice in the manufacture of autoclaved-based building products due to the accelerated formation of 1.1 nm tobermorite which is regarded among the most important of the hydrous calcium silicate phases (Taylor, 1997). Clay-brick waste, rich in $Al_2O_3$ and $SiO_2$, is generated during production, transportation and construction and demolition (C&D) procedures in enormous quantities worldwide. The opportunities to develop novel applications for this otherwise discarded material consequently has global significance. Addition of finely ground fired clay-brick to blends of Portland cement and quartz sand has been shown to enhance the formation of tobermorite (Klimesch & Ray, 2001), the principal binder of most autoclaved calcium-silicate based materials. Using a combination of techniques this paper examines the behaviour of clay-brick fines, as an alternate aluminosilicate source for cement-based materials cured under hydrothermal conditions. In order to investigate the effectiveness of clay-brick commonly employed kaolin-based filler was used as a comparison.

## 2. EXPERIMENTAL

The following 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 m²/kg 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 particle diameter predominantly finer than 75 micron and a Blaine surface area of 360 m²/kg was sourced from Unimin Australia Limited, Sydney, Australia.

- Clay-brick (CB) 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). using ICDD-JCPDS Powder Diffraction patterns. The major crystalline phases in decreasing order of abundance were: quartz, mullite, hematite, cristobalite and rutile.

- A commercially available kaolin-based filler containing $SiO_2$ 24.7%, CaO 0.1%, $Al_2O_3$ 49.5%, $Fe_2O_3$ 0.4%, $K_2O$ 2.4%, $TiO_2$ 1.5%, MgO 0.4%, $Na_2O$ 0.2%.

Control blends were prepared using cement: quartz ratios of 40:60 comparable to those used in the buildings product industry. Kaolin-based filler and/or clay-brick waste was introduced at 4.3 wt % quartz replacement. Table 2 contains the chemical composition

**Table 1:   Major oxide composition of brick fines from XRF analysis.**

| Major oxides | % wt |
|---|---|
| $SiO_2$ | 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 hours.

of the blends studied. Water-to-total solids ratio (w/s) of 0.33 was used as this yielded similar workability for all the mixtures. Mechanical mixing of these blends was conducted in accordance with ASTM C305-99 with minor modification. Pastes were cast into stainless steel moulds and consolidated on a vibratory table, followed by precuring for 24 hours in a moist cabinet. For each mix three 50 × 50 × 50 mm cubes were cast. Demoulded cubes were autoclaved at 180 °C for 8 hours and were then allowed to air dry at ambient temperature for 48 hours prior to mechanical testing. The bulk density of cubes was determined by weight and volume measurements. Compressive strength was measured according to ASTM C109-02. The specimens were loaded under compression until failure using a Tinius Olsen instrument. After mechanical testing samples were oven dried overnight at around 105 °C followed by disc milling. The average compressive strength of all acceptable specimens per mould, at the same test age, is reported to the nearest 0.1 MPa.

A TA Instruments SDT 2960 simultaneous DTA-TGA analyser 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 under flowing air at 20 mL/min from 25 to 1000 °C. DTA-TGA 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.

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 $CuK_\alpha$ radiation ($\lambda$ = 0.1540981 nm). Samples were mounted in plastic sample holders. The holder and sample were placed on the diffractometer and an XRD pattern collected for 2θ values from 3.000° to 65.000°, at intervals of 0.020°. Step times of 6 seconds 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 integrated peak heights and areas (Cheary & Coelho, 1992).

The amount of acid insoluble residue (AIR) was determined by a modified filtration method and provided a measure of the total unreacted material. The residues 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.

## 3.   RESULTS AND DISCUSSION

Table 3 and Figure 1 show the changes in compressive strength with the addition of kaolin-based filler and CB as silica replacement.

The average compressive strength was found to increase with the inclusion of additives. The higher compressive strength may be attributed to the formation of more hydration products; a reduced amount of OPC reduces the availability of CH for hydration reactions. Quartz replacement ensures the effectiveness of siliceous additives, as pozzolans in increasing compressive strength will not suffer as a result of CaO reduction. The use of clay filler does not have detrimental effect on strength. Both the CB and kaolin-based additive have comparable, if not greater strength than the control formulations. This suggests that the nature and quantity of principal phases, namely $Al_2O_3$ and $SiO_2$, have a significant effect on phase development.

Table 4 provides a summary of the crystalline phases identified by X-ray diffraction in Figure 2. C-S-H with main d-spacings at around 0.304 and 0.73 nm and referred to as "fibrous C-S-H" was detected in all samples (Kalousek, 1955). The XRD peak in the 0.300 nm region due to $CaCO_3$ interferes with reflections attributable to C-S-H. The presence of CH or $\alpha$-$C_2SH$ was not

**Table 3:   Average compressive strength values for autoclaved blenFig. 1 Average compressive strength values for autoclaved blends.**

| Sample | Total $Al_2O_3$ (%) | Compressive Strength (MPa) |
|---|---|---|
| Control | 2.16 | 65.1 ± 3.3 |
| Kaolin | 4.26 | 71.7 ± 3.6 |
| CB | 2.94 | 71.8 ± 2.1 |

**Table 2:   Chemical composition of pastes studied.**

| Sample | Cement:Silica Ratio | Atom Ratio Ca/Si | Atom Ratio Ca/ (Al+Si) | Atom Ratio Al/ (Al+Si) | Atom Ratio Al/Si |
|---|---|---|---|---|---|
| Control | 0.67 | 0.41 | 0.39 | 0.036 | 0.04 |
| Kaolin | 0.72 | 0.43 | 0.40 | 0.073 | 0.08 |
| CB | 0.72 | 0.42 | 0.40 | 0.050 | 0.05 |

**Table 4:   Phases and integrated peak areas identified by XRD.**

| Sample | Quartz 0.334 nm | Tobermorite 1.1 nm | Hydrogarnet 0.505 nm | CaCO$_3$ 0.303 nm |
|---|---|---|---|---|
| Control | 2076.98 | 71.26 | 22.16 | 161.64 |
| Kaolin | 1928.98 | 205.57 | 39.57 | 150.64 |
| CB | 2088.36 | 83.76 | 18.97 | 163.34 |

**Table 5.   Crystallite size of tobermorite.**

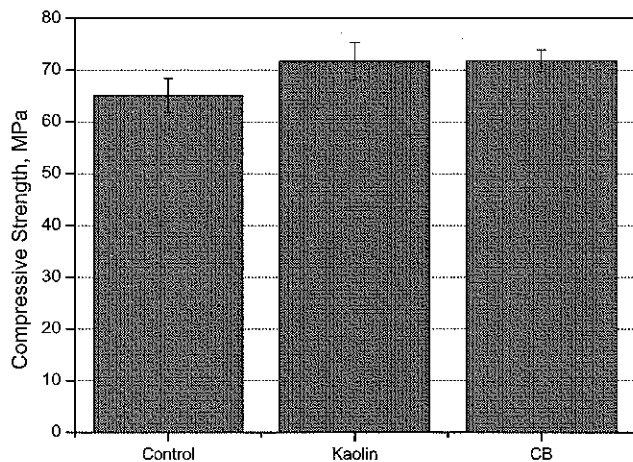| Sample | Crystallite size (nm) | | |
|---|---|---|---|
| | [001] | [110] | [111] |
| Control | 26 | 28 | 12 |
| Kaolin | 32 | 34 | 26 |
| CB | 35 | 29 | 18 |

detected in any samples; these phases are consumed or avoided respectively with the addition of large amounts of quartz. The absence of kaolin and mullite (from CB) indicates these phases were completely consumed.

The increase in compressive strength is attributed to the formation of calcium silicate hydrates, in particular crystalline tobermorite. The identification of tobermorite is based on the three strongest XRD lines of this phase or d-spacings, 1.1, 0.308 and 0.297 nm. The stronger basal reflections of tobermorite indicate that with the addition pozzolanic material the blends are enriched in 1.1 nm tobermorite, the most important of the calcium silicate hydrate phases formed during autoclaving. Table 4 reveals the kaolin-based addition is superior in the formation of 1.1 nm tobermorite in comparison to CB. This is considered to be due to the higher quantity of Al present in the kaolin-based filler as listed in Table 3.

An increased amount of hydrogarnet is also observed with kaolin-based filler incorporation. The presence of hydrogarnet is known to adversely affect strength (Bessey, 1964; Stebnicka, 1980) and it is therefore noteworthy that less hydrogarnet is formed with the addition of CB than in the kaolin specimen and the control. The formation of hydrogarnet can be explained in terms of the reacted starting materials. At higher Al contents hydrogarnet will persist because coexisting Al-containing phases have a limited capacity to incorporate Al.

It has been firmly established that hydrogarnet always forms first along with CH and C-S-H (Klimesch & Ray, 1998; 1999). With continued hydrothermal treatment, the onset of hydrogarnet decomposition was found to coincide with the appearance of Al-tobermorite. It was also demonstrated by these authors that hydrogarnet supplies most if not the entire Al for the formation of Al-tobermorite.

The above-mentioned reflections of 1.1 nm tobermorite were used for the calculation of the crystallite size (Table 5). The dimensions of the control blend for both formulations are initially of a similar nature. With the inclusion of the kaolin-based filler the crystallite

size increases noticeably in all three directions. The CB also causes a crystallite size change, however the differences are much less pronounced in both the [110] and [111] direction.

Differential thermal (DT) curves of autoclaved specimens are depicted in Figure 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$_5$S$_6$H$_5$) where present; |
| ca. 260° to 350 °C (endo) | presence of a member of the hydrogarnet series, C$_3$AS$_{3-x}$H$_{2x}$, x = 0 to 3; |
| ca. 573°C (endo) | crystalline inversion due to unreacted quartz (Q); |
| ca. 650° to 780 °C (endo) | decarbonation of CaCO$_3$; |
| ca. 850° to 900 °C (exo) | crystallization of b-wollastonite (b-CS) from C-S-Hs including (C$_5$S$_6$H$_5$) where present. |

The endotherm attributed to hydrogarnet, between 260 and 350 °C in the DT curves of Figure 6, was not discernable for the control or the CB specimens as this phase was only formed in trace amounts.

Table 6 outlines the results of analysis of the exotherm above 800 °C due to the crystallisation of beta-wollastonite (b-CS). An increase in the b-CS formation temperature has been correlated with an increase Al content in tobermorite, furthermore the exotherm became flatter and broader (Kalousek, 1957).



**Figure 1:   Average compressive strength values for autoclaved blends.**
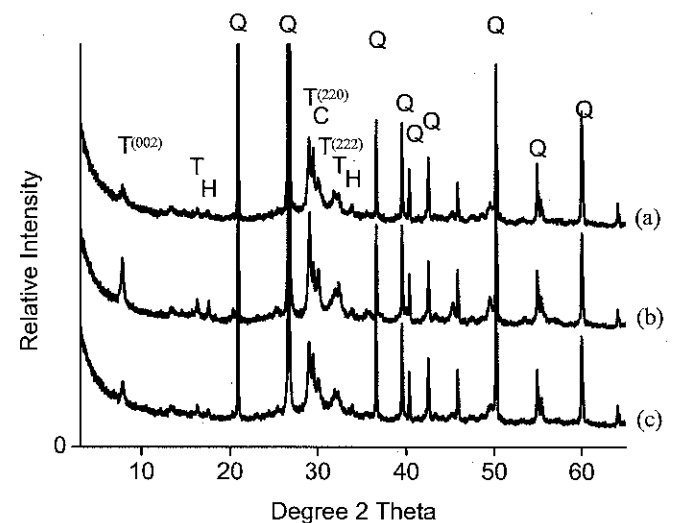


**Figure 2:   Powder x-ray diffraction pattern of autoclave cured specimens: (a) control; (b) kaolin; and (c) CB. T = tobermorite, H = hydrogarnet, Q = quartz, C = calcite.**

**Table 6:    Variation in the β-CS exotherm for autoclaved cement blends.**

| Sample | Exotherm | |
|---|---|---|
| | Temp (°C) | Height |
| Control | 845 | 167 |
| Kaolin | 853 | 84 |
| CB | 846 | 163 |

**Table 7:    AIR Data.**

| Sample | Bulk | | Combined/ Reacted | | % Combined/ Reacted | |
|---|---|---|---|---|---|---|
| | $Al_2O_3$ | $SiO_2$ | $Al_2O_3$ | $SiO_2$ | $Al_2O_3$ | $SiO_2$ |
| Control | 2.16 | 67.34 | 1.94 | 31.50 | 90.00 | 46.78 |
| Kaolin | 4.26 | 64.15 | 3.89 | 28.72 | 91.22 | 44.78 |
| CB | 2.94 | 66.08 | 2.28 | 32.32 | 77.64 | 48.91 |

The results suggest increased alumina incorporation in samples autoclaved with the addition of clay-based filler, the kaolin-based filler promoting the greatest inclusion of Al into the tobermorite lattice structure.

Results of the analysis of the bulk and combined AIR compositions are shown in Table 7. The availability of CaO with the addition of either kaolin or CB remained constant due to quartz replacement, however the bulk $Al_2O_3$ increased and $SiO_2$ decreased.

From the combined or reacted oxide content, it is clear that both sources of additional alumina were reactive in the autoclave environment. Over 90 percent of the available alumina with kaolin-based filler addition was incorporated into hydration phases formed. This level is similar to the alumina supplied solely by the OPC in the control. CB addition, although resulting in a total combined increase in alumina, exhibited incorporation of only 78 percent, a level much lower than was potentially possible. The alumina supplied by the kaolin-based filler appears to be more reactive that CB alumina; this is most likely due to the crystallinity and stability of the alumina containing phase (Baronio and Binda 1997).

Although the silica content of the CB and kaolin samples is found to decrease in comparison to the control, the amount
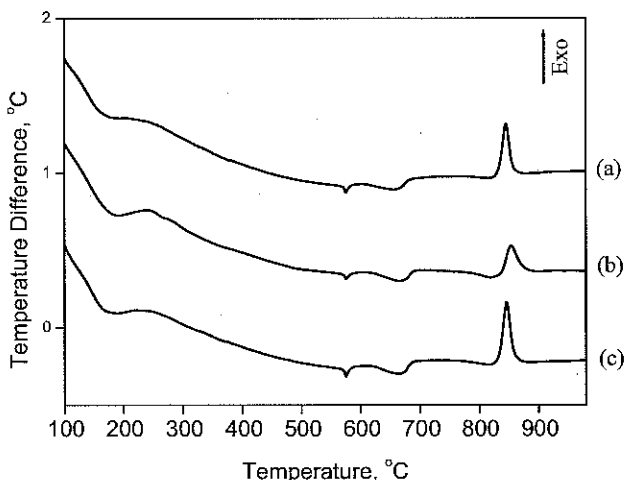


**Figure 3:    DT curves of (a) control; (b) kaolin; and (c) CB.**

or percentage of combined silica, is superior for the CB. The siliceous material introduced with CB addition is therefore more reactive than that which it replaces in both the control and kaolin-based filler.

## 4.  CONCLUSION

From a combination of DTA-TGA, XRD and AIR the following can be concluded:

Finely ground fired clay-brick represent an effective aluminosilicate source for use in autoclave cured cementitious materials producing strength equivalent to that of typically used kaolin-based fillers employed in industry.

Clay-brick fines promoted the formation of hydrous calcium silicate phases, in particular 1.1 nm tobermorite. The amount of hydrogarnet was reduced to a minimum possibly due to the greater reactivity of the siliceous source in fired clay-brick in comparison to the kaolin-based material.

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