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STRENGTH DEVELOPMENT IN HYDROTHERMALLY TREATED OPC:CB SYSTEMS

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The strength developments of hydrothermally cured blends comprised of ordinary Portland cement (OPC) and clay-brick waste (CB) and treated at 180°C under saturated steam for 6 h were studied. Two types of CB, of different chemical and mineralogical make-up, were used to make OPC-CB blends where 10 to 80 mass% CB replaced OPC. The nature of the hydration products formed after autoclaving were subsequently investigated by using a combination of DTA, DTG, TG, X-ray diffraction, and wet chemical techniques. The modes of the hydrothermal reactions between OPC and the two types of CB, as well as the nature of the main binder belonging to the tobermorite family, are discussed and related to the development of the strength of the autoclaved articles.

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

Introduction

In recent years worldwide attention has been directed towards developing new technologies and methods for the utilization and recycling of clay-brick waste (CB) into renewable construction materials. Previous studies have shown that CB exhibits pozzolonic characteristics and, therefore, it is feasible to partially replace cement with CB [1]. Although CB and OPC are compositionally compatible, with CB being rich in SiO_2 and Al_2O_3 and lean in CaO, while the opposite holds for, the oxide make-up is composed of the same main oxides, however in different proportion and mineralogical composition. These differences play important role during the formation of the binder (calcium silica hydrates (CSH)).

Hydrothermal curing or autoclaving is a proven and widely used process for the manufacture of cement based building products incorporating waste materials such as fly ash and blast furnace slag. Autoclaving enhances the reactivity of the starting raw materials because of the relatively high temperatures. In the production of cement-based building products such as dense and aerated concretes, thermal insulation boards, and fiber-reinforced cement products, autoclaving provides several advantages over air curing including: the development of permanent high early strength within a few hours, a reduction in the drying shrinkage, and a superior resistance to chemical attacks i.e. carbonation and sulphate attack [2, 3].

The phases formed at the completion of autoclaving depend largely on the starting raw materials used. Previous work by the present authors showed that formation of 1.1 nm tobermorite (tobermorite), regarded as the principal binder of most autoclaved calcium silicate based building materials, is enhanced by the addition of finely ground clay-brick to blends of OPC and quartz [4–6]. Specifically, CB plays a significant role in the formations of tobermorite and hydrogarnet, which are critical phases in relation to both strength and durability. From the viewpoint of durability, the resistance to carbonation and lower drying shrinkage, hydrogarnet $C_3AS_{3-x}H_{2x}$ with x=0 to 3 is considered important [7], where C=CaO, A=Al_2O_3, S=SiO_2, H=H_2O.

The aim of this work is to study the strength development in connection to the nature of hydration products formed after autoclaving in the OPC:CB blends using a combination of DTA, DTG, TG, X-ray diffraction, and wet chemical techniques. In addition, this work investigates relationship between strength development and binder crystallinity.

Experimental

The following raw materials were used:

- Goliath cement (OPC) containing SiO_2 20.0%, CaO 64.2%, Al_2O_3 4.5%, Fe_2O_3 3.7%, SO_3 3.5%, and having a fineness index (Blaine) of 350 m^2 kg^{-1} was produced by Australian Cement, Auburn, NSW, Australia. The OPC was blended with 5 mass% calcium carbonate ($CaCO_3$).
- Two types of CB waste passing 2.38 mm denoted high alumina (CB1) and extruded (CB2), were obtained from major CB manufacturers in Sydney, Australia. Dry ball milling method of pre-screened,

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crushed material was employed to produce ground CB having a particle size distribution comparable to that of quartz sand used by the industry. Table 1 depicts the major oxides of the two CB types as determined by X-ray fluorescence (XRF). The mineralogical compositions were determined qualitatively using X-ray powder diffractometry (XRD). Crystalline phases were identified using JCPDS powder patterns and are summarized in Table 2, in decreasing order of abundance.

OPC:CB blends were prepared using a water-to-total solids ratio (*w/s*) of 0.35 as this yielded comparable workability for all the mixtures. CB was added at 10, 20, 30, 40, 50, 60, 70 and 80 mass% as cement replacement. The bulk Ca/Si and Ca/(Al+Si) atom ratios for the different blends are given in Table 3. Mechanical mixing was conducted in accordance with ASTM C 305-082 [8]. Pastes were cast into stainless steel moulds and consolidated on a vibratory table, followed by a 24 h curing period in a moist cabinet. Demoulded specimens were autoclaved for 7.5 h, 6 h of which were at 180°C under saturated steam. After autoclaving specimens were allowed to air dry for 2 days, followed by compressive strength testing according to ASTM C109-02 [9]. The specimens were loaded under compression until failure using a Tinius Olsen testing machine. Compressive strength results are reported to the nearest 0.1 MPa. After compressive strength testing, crushed specimens were dried at around 105ºC overnight followed by disc milling for further evaluations using a combination of DTA-TG, XRD and wet chemical analysis to characterise the nature of the hydration products formed. Thermal analyses on powdered samples were preformed using a TA Instruments SDT 2960 simultaneous DTA-TG analyser at a heating rate of 10 K min^{-1} from 20 to 1000°C under flowing air (20 mL min^{-1}). Sample sizes of 30 to 50 mg were packed into a Pt–Rh crucible with 20 taps. The thermal data were evaluated using the TA Instruments data analysis software as detailed by Klimesch and Ray [10]. XRD analysis on powdered specimens were carried out using a Siemens D5000 diffractometer and copper $K_{\alpha 1}$ radiation from 3 to 60º 2θ at 0.02° 2θ s^{-1}. The amount of acid-insoluble residue (AIR) was used as a measure of total unreacted material, according to the modified method described by Klimesch and Ray [11]. In addition, the residues from triplicate AIR analyses were combined and the chemical composition determined by Inductively Coupled Plasma Optical Emission Spectrometry (ICP) by Genalysis Laboratory Services Pty. Ltd., Western Australia.

The chemically bound water was determined from TG mass losses as described by Bhatty and Reid [12] with modifications using Eq. (1):

$$\text{chemically bound water}=L_{\text{dh}}+L_{\text{dx}}+0.41(^*L_{\text{dc}}) \quad (1)$$

where L_{dh} is dehydration between ~103 to 440°C, L_{dx} is dehydroxylation between ~440 to 580°C, $^*L_{\text{dc}}$ is decarbonation between ~580 to 1000°C corrected for calcite presence in OPC and factor 0.41 corrects for water loss equivalent to that of decarbonation occur-

Table 1 Chemical composition of CB types used in this investigation. Oxides are in mass%

Oxide	CB1	CB2
SiO_2	53.36	65.30
Al_2O_3	41.44	18.79
Fe_2O_3	1.40	7.10
CaO	1.04	1.56
MgO	0.23	1.34
K_2O	0.56	2.11
Na_2O	0.27	0.62
TiO_2	1.25	0.81
LOI*	0.17	0.92

*loss on ignition at 1050°C for 2 h

Table 2 Crystalline phases present in CBs in decreasing order of abundance

CB1	CB2
mullite	quartz
cristobalite	mullite
quartz	hematite
andalusite	rutile

Table 3 OPC:CB ratio, bulk Ca/Si and Ca/(Al+Si) atom ratios of studied blends

CB added/%	OPC:CB ratio	Bulk Ca/Si atom ratios		Bulk Ca/(Al+Si) atom ratios	
		CB1	CB2	CB1	CB2
10	9.00	2.66	2.53	1.88	1.97
20	4.00	2.07	1.91	1.36	1.47
30	2.33	1.62	1.45	1.00	1.11
40	1.50	1.25	1.10	0.74	0.84
50	1.00	0.95	0.83	0.55	0.62
60	0.67	0.70	0.60	0.39	0.46
70	0.43	0.49	0.42	0.27	0.32
80	0.25	0.31	0.27	0.17	0.20

ring in this region, assuming that the carbonate was formed by carbon dioxide reacting with calcium hydroxide (CH) present during hydration.

It is to be noted, that in the presence of α-C_2SH, the mass loss due to CH is subject to overlap. Additionally, dehydration of C–S–Hs may also be subject to overlap, as C–S–Hs are known to dehydrate gradually and variably over wide temperature ranges [13].

Ca/Si atom ratio of binding material was calculated using Eq. (2):

$$\text{Ca/Si atom ratio}= \text{mol CaO of binding material/reacted mol } SiO_2 \quad (2)$$

where Eq. (3) was employed when CH and α-C_2SH were present and Eq. (4) when they were absent; reacted mol SiO_2 was calculated according to Eq. (5):

$$\text{mol CaO in binding material}= \text{bulk CaO}-(4.11L_{dx}+1.68{*}L_{dc})\cdot 0.76 \quad (3)$$

where factors 4.11, 1.68 and 0.76 correct for CH formed during hydroxylation and decarbonation and CH amount equivalent to CaO, respectively;

$$\text{mol CaO in binding material}= \text{bulk CaO}-1.27L_{dc} \quad (4)$$

where factor 1.27 corrects for equivalent to that of decarbonation occurring in this region, assuming that the carbonate was formed by carbon dioxide reacting with calcium hydroxide (CH) present during hydration.

$$\text{reacted mol } SiO_2= \text{bulk } SiO_2-(SiO_2 \text{ in AIR, ICP}) \quad (5)$$

Results and discussion

Kinetics of hydration

DTA curves for CB1 and CB2 series are shown in Figs 1 and 2, respectively. The main observed endotherms (endo) and exotherms (exo) are ascribed to:

ca. 105 to 260°C (endo) not shown	dehydration reactions of calcium silicate hydrates (C–S–Hs) including 1.1 nm tobermorite ($C_5S_6H_5$) where present
ca. 260 to 350°C (endo) not shown	dehydration reactions of a member of the hydrogarnet series, $C_3AS_{3-x}H_{2x}$, x=0 to 3
ca. 440 to 580°C (endo)	dehydroxylation reactions of CH including α-C_2SH at ca. 500 to 550°C where present
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 β-wollastonite (β-CS) from C–S–Hs including ($C_5S_6H_5$) where present

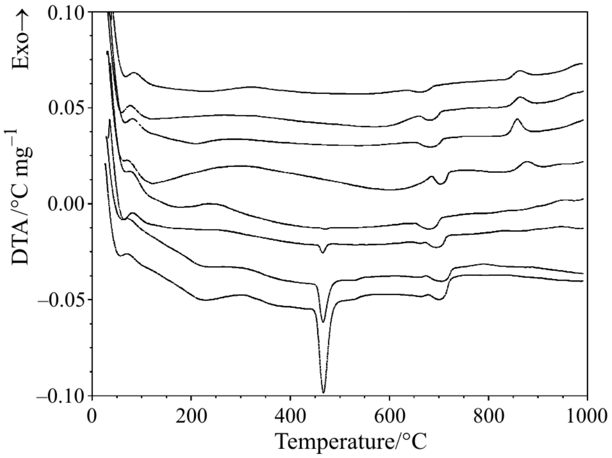

Fig. 1 DTA curves of CB1 series for 10 to 80 mass% CB1 additions from bottom to top

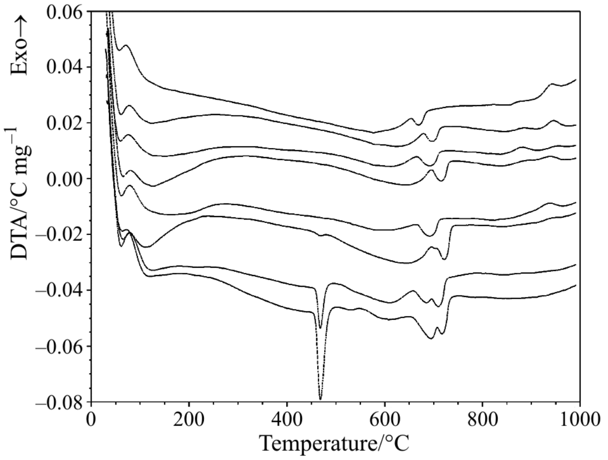

Fig. 2 DTA curves of CB2 series for 10 to 80 mass% CB2 additions from bottom to top

Results for chemically bound water, combined SiO_2 and calculated Ca/Si atom ratio of the binding material are depicted in Figs 3 to 5. The combined data show that increasing CB additions enhanced the rate of the lime-silica reaction with the CH content continuously decreasing with increasing amounts of CB added and finally disappearing beyond 30 mass% (Figs 1 and 2). Overall the chemically bound water varied slightly up to 40 mass% additions, followed by a continuous decrease with further CB additions (Fig. 3). The amount of combined silica increased up to 40 to 50 mass% additions for CB2 and CB1 series respectively, followed by a decrease at greater additions (Fig. 4). Consequently, the calculated Ca/Si atom ratio of the binding material showed a continuous decrease as evidenced in Fig. 5, indicating that the ratio of crystalline/amorphous content of the binder increased [14]. In other words, a transformation of lime-rich phases into more crystalline, low-lime phases occurred as sup-

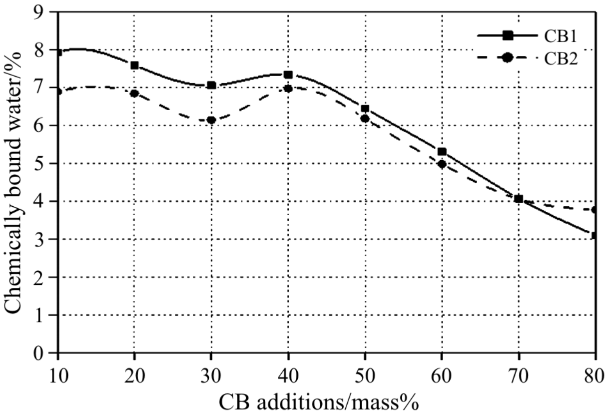

Fig. 3 Chemically bound water amount of autoclaved OPC:CB blends

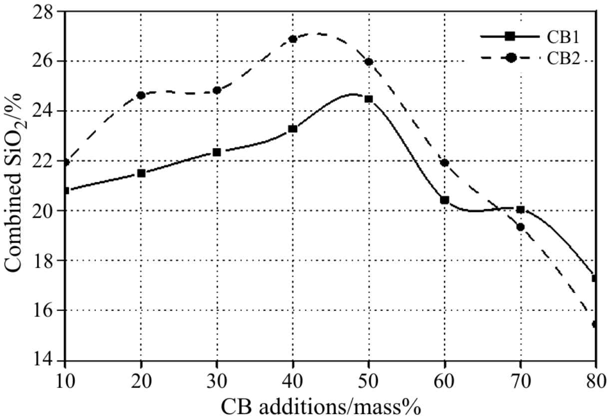

Fig. 4 Combined SiO_2 amount of autoclaved OPC:CB blends

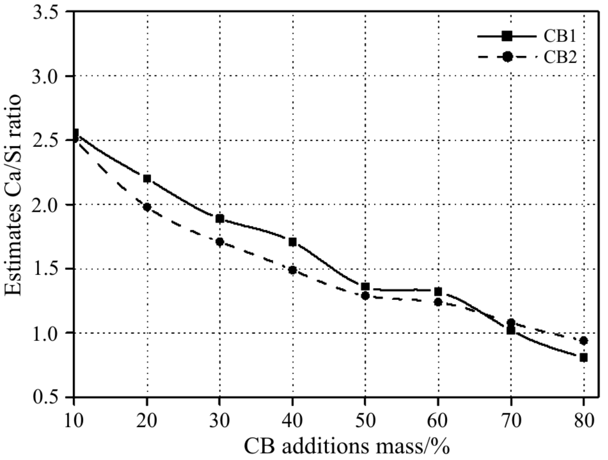

Fig. 5 Estimated Ca/Si atom ratio of the binding material

ported by DTA (Figs 1, 2 and 6) and XRD data. Specifically from XRD data, the (002) peak of tobermorite was very weak and broad for 30 mass% addition reaching a maximum at 50 mass% addition followed by a sharp decrease and was no longer discernible at 80 mass% addition for the CB1 specimens. In contrast, for the CB2 specimens the (002) peak of tobermorite reached a maximum at 40 mass% addition followed by a steady decrease at greater additions. Maximum tobermorite amounts, therefore, agree well with the maxima combined silica amounts (Fig. 5).

Strength development

The variation in the compressive strength with CB type and the amount is shown in Fig. 6. The lower strengths for 10 to 30 mass% CB additions are attributable to the presence of CH and α-C_2SH (Figs 1 and 2), the latter known to be a low strength giving phase [15, 16]. The strength increase beyond 30 mass% CB additions is attributable to, amongst other, the presence of crystalline tobermorite reaching a maximum at 40 and 50 mass% additions for CB2 and CB1, respectively followed by a decrease at greater additions. It is to be noted that there exists good correlation between the combined SiO_2 amount and compressive strength, the former reaching maxima at 40 and 50 mass% additions for CB2 and CB1, respectively (Fig. 5). Beyond the optimum of 50 mass% CB additions, the availability of CaO from cement decreased, as evidenced by the decreasing OPC:CB ratio (Table 3), resulting in the formation of fewer hydration products, and further additions of CB acted only as a diluent. This view is supported by the noted decrease in both the chemically bound water (Fig. 4) and combined SiO_2 (Fig. 5) amounts. From the viewpoint of strength development, it may be concluded that since the particle size distributions of the two CB types were comparable, it follows that CB mineralogy and chemical make-up are important factors in relation to strength development (Tables 1 and 2). Our findings demonstrate that the optimum amount of CB type should be experimentally determined in situ.

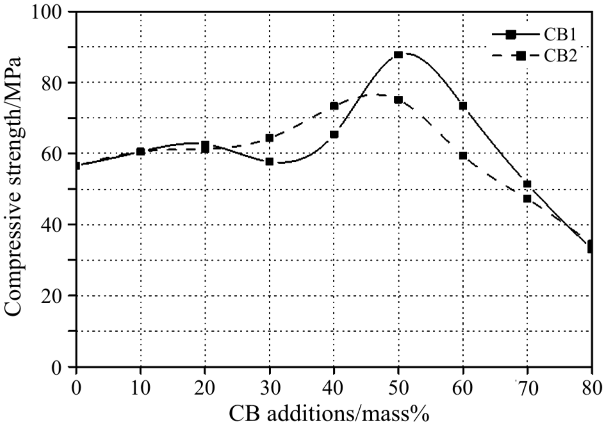

Fig. 6 Average compressive strength of autoclaved OPC:CB blends

Conclusions

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

- The use of clay-brick fines in combination with OPC for the production of hydrothermally cured calcium silicate based materials is a viable option for the future.
- The addition of CB up to 50% accelerates the rate of lime-silica reaction. This is confirmed by increasing amounts of combined silica and a decrease in free lime content.
- The transformation of the lime-rich phases into more crystalline, low-lime phases is manifested by decreasing Ca/Si atom ratio of the total binding material and increasing strength.
- The optimum amount of CB type should be determined in situ.
- There exists a good correlation between the maximum compressive strength and the maximum amount of combined silica.

Acknowledgments

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References

1 S. Wild, A. Gailius, H. Hansen, L. Pederson and J. Szwabowski, Copernicus Research Project: Recycling of Waste Clay Brick and Tile Material for the Partial Replacement of Cement in Concrete, European Commission, Brussels 1995–1998.

2 H. F. W. Taylor, Cement Chemistry, 2nd Ed., Thomas Telford, London 1997.

3 G. L. Kalousek, Proc. 5th Intern. Symp. Chemistry of Cements, Vol. 3, Tokyo 1969, pp. 523–537.

4 D. S. Klimesch and A. Ray, Incorporating brick fines in cement based building materials, In: Figueiras *et al*. (Eds), Proceedings of the International Conference on Composites in Construction, Porto 2001, pp. 47–49.

5 D. S. Klimesch, A. Ray and J. P. Guerbois, Thermochim. Acta, 389 (2002) 195.

6 D. S. Klimesch, A. Ray and M. Gutovic, An investigation of the behaviour of different waste fired-clay products in autoclaved cement:fired-clay products. In: International Conference on Sustainable Waste Management and Recycling: Challenges and Opportunities. Kingston University, London, (accepted 2004).

7 H. F. W. Taylor, Cement Chemistry, 2nd Ed., Thomas Telford, London 1997.

8 Standard Practice for Mechanical Mixing of Hydraulic Cement Pastes and Mortars of Plastic Consistency. In: ASTM C 305-99, 1999, ASTM International: Philadelphia.

9 Standard Test Method for Compressive Strength of Hydraulic Cement Mortars (Using 2-in. or 50-mm Cube Specimens). In: ASTM C 109/C 109M-02. 2002, ASTM International: Philadelphia.

10 D. S. Klimesch and A. Ray, Thermochim. Acta, 289 (1996) 41.

11 D. S. Klimesch and A. Ray, Adv. Cem. Res., 9 (1997) 157.

12 J. I. Bhatty and J. K. Reid, Thermochim. Acta, 91 (1985) 95.

13 Y. Okada, K. Sasaki, B. Zhong, H. Ishida and T. Mitsuda, J. Am. Ceram. Soc., 77 (1994) 1319.

14 J. M. Crennan, J. R. L. Dyczek and H. F. W. Taylor, Cem. Concr. Res., 2 (1972) 277.

15 G. L. Kalousek, J. Amer. Concr. Inst., 26 (1955) 989.

16 J. L. R. Dyczek and H. F. W. Taylor, Cem. Concr. Res., 1 (1971) 589.