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Sustainable infrastructure development through use of calcined excavated waste clay as a supplementary cementitious material

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Abstract

Major infrastructure development projects in London produce large quantities of London clay and use significant volumes of concrete. Portland cement (CEM I) in concrete is normally partially replaced by supplementary cementitious materials such as ground granulated blastfurnace slag or pulverised fuel ash. The supply of supplementary cementitious materials is critical to the production of sustainable concrete. This study has investigated use of waste London clay as a supplementary cementitious material. The optimum calcined clay was produced at 900°C and concrete made with 30 wt.% of CEM I replaced by calcined clay had 28-day strengths greater than control samples. Compressive strengths of concrete containing calcined London clay were similar to concrete containing ground granulated blastfurnace slag and pulverised fuel ash. The production of calcined London clay emits ~70 kg CO₂/tonne and this is 91% lower than CEM I. 30 wt.% replacement of CEM I by calcined London clay therefore produces concrete with ~27% lower embodied carbon. London clay can be calcined to form a technically viable supplementary cementitious material and use of this in concrete would enable major civil infrastructure projects to contribute to a circular economy.

Keywords: calcined clay; supplementary cementitious materials; pozzolan; cement; concrete

1. Introduction

Major civil infrastructure projects in and around London produce huge quantities of waste London clay. For example, Crossrail, the new east-west London rail line, involved excavating 42 kilometres of tunnels and 14 kilometres of stations and interchange tunnels (Crossrail, 2015), and generated in excess of 7 million tonnes of tunnelling spoil, mainly consisting of London clay. The majority of the excavated clay was used in a wetland nature reserve, in land raising schemes, a golf course development and in the restoration of old landfill sites (Crossrail, 2015b). Future projects that will be generating significant quantities of waste London clay include Crossrail II, the Thames Tideway Tunnel, the new Silvertown Tunnel and the HS2 high-speed rail link.

Pozzolans are siliceous/aluminous material that when finely divided, react with calcium hydroxide in the presence of water to produce compounds that have cementitious properties (Sabir et al., 2001). Metakaolin has many benefits when used as a supplementary cementitious material (SCM) in concrete, including lower heat of hydration, higher density, improved strength and improved resistance to degradation mechanisms (Siddique and Klaus, 2009; Wild and Khatib, 1997). Large deposits of high-purity kaolinite are rare and the vast majority of natural clay deposits (including London clay) contain kaolinite with other less reactive clay minerals (e.g. montmorillonite and illite) and impurities such as quartz and feldspar. Removing these impurities is energy intensive and expensive. High-purity metakaolin is not widely used as a SCM despite proven advantages. Low-grade/purity natural clays produce a less reactive pozzolan but their use in concrete is not well-established.

The drive to reduce environmental impact and the need for cleaner production of sustainable construction and infrastructure development is increasing. Potentially economically viable eco-efficient cements have been reviewed and this highlighted the importance of clinker substitutes and SCMs in future Portland cements (UNEP, 2016). The vast majority of concrete is already made with Portland cement partially replaced by SCMs, and normally this is ground granulated blastfurnace slag (GGBS) or pulverised fuel ash (PFA) (Mikulčić et al., 2016). GGBS is a by-product from the steel industry and PFA is produced from coal-fired power stations. The use of these SCMs enhances the physical and chemical properties of concrete (Paris et al., 2016) and also addresses environmental issues associated

with energy and waste management (Aprianti, 2017). However, the future availability of the SCMs GGBS and PFA does not match worldwide demand for concrete (Benhelal et al., 2013; Schneider et al., 2011). The supply of SCMs in London is becoming a critical barrier to producing more sustainable concrete (Mann, 2014; IEA, 2009).

London clay is readily available from local infrastructure development projects and does not have the supply issues associated with GGBS and PFA. It has potential, through reuse as an SCM, to be part of a circular economy, which is an economy that keeps materials in the economic cycle so they retain value, rather than being part of a linear economy in which they become waste.

The significance of this research is that for the first time London clay, which is available in significant quantities, has been assessed as a raw material to manufacture calcined clay for use as an alternative SCM in concrete. We believe this is highly significant research that beneficially reuses a waste and potentially solves the SCM supply issue in a major world city. Excavated London clay obtained from Crossrail has been obtained and heated to between 600°C and 1000°C. The pozzolanic activity of the calcined clays formed by the thermal treatment has been investigated. The optimum calcined London clay has then been blended with CEM I at three different replacement levels (10, 20, 30 wt.%) and used to produce concrete with water-to-binder ratios of 0.3, 0.4 and 0.5. The effect of calcined London clay on concrete workability and strength is reported and the results are compared to control samples containing GGBS, PFA and silica fume (SF). The carbon emissions associated with calcined London clay are calculated, and the viability of producing SCMs from calcined London clay is discussed.

2. Materials and Methods

2.1. Materials

Waste London clay was supplied from Crossrail (Pudding Mill Lane site in East London) (Crossrail, 2014). The chemical composition of dried clay was analysed by x-ray fluorescence (XRF, AXS S4 explorer, Bruker, USA) using an Rh source at 1kW. Crystalline phases were determined by x-ray diffraction (XRD, PANalytical X-Pert Pro MPD diffractometer, Philips, Netherlands) using Cu K α

radiation operated at 40 kV and 40 mA. Samples were scanned between 5° and 70° 2 θ using a step size of 0.0167° 2 θ using 30s per step. Thermogravimetric analysis (TGA) of as-received clay used a heating rate of 10°C/min from 30 to 1000°C (Polymer Laboratories Thermal Science STA 1500 analyser) with a N₂ flow rate of 30 ml/min in the heating chamber to avoid carbonation.

CEM I 42.5 N conforming to BS EN 197-1 (Hope Construction Materials, UK) was used in all mixes. The mineralogical composition, calculated using Bogue's equation, was 61.5% C₃S, 13.8% C₂S, 7.1% C₃A and 8.2% C₄AF. Thames Valley gravel (Travis Perkins, UK) with a specific gravity of 2.42 and particle size < 14 mm was used as coarse aggregate. The moisture content and water absorption was 0.49% and 3.06% respectively. Silica sand (Travis Perkins, UK) with particles <5 mm was used as fine aggregate. This had specific gravity, moisture content and water absorption of 2.58, 0.44% and 0.63% respectively (ASTM C127-15, ASTM C128-15). Particle size distribution of the fine and coarse aggregate are presented in Table 1.

PFA, GGBS and silica fume (SF) were supplied by Lafarge Tarmac. The PFA had a median particle size of 15.2 μ m (laser diffraction particle size analysis, LS 100, Coulter, USA) and specific gravity of 2.43 (gas displacement pycnometer, AccuPyc, Micromeritics, USA). The GGBS had a median particle size of 16.1 μ m and specific gravity of 3.06. The SF powder had a median particle size of 116.2 μ m and specific gravity of 2.38. The oxide composition of CEM I, as-received London clay, GGBS, PFA and SF, determined by XRF, are presented in Table 2.

2.2. Calcined London clay

London clay was formed into lumps (~ 1 cm diameter) and oven-dried at 105°C for 24 hours. The hard clay nodules formed were ground in a disc mill (Gy-Ro, Glen Creston Ltd, UK) for 1 minute and the dry clay powder produced calcined at 600°C, 700°C, 800°C, 900°C and 1000°C using an alumina crucible in an electric chamber furnace (Carbolite, UK). The temperature was increased to the calcining temperature at 5°C/min and maintained for 2 hours. Calcined clay samples were then ground in the disc mill for 2 minutes, to produce <100 μ m powder.

Calcined clays were characterized using thermogravimetric analysis (TGA), Fourier transform infrared (FTIR) spectroscopy, XRD for crystalline phases, particle size distribution (laser diffraction),

density (pycnometry) and BET surface area (TriStar 3000, Micromeritics, USA). FTIR used a Nicolet 6700 spectrometer (Thermo Scientific) with an IR source, KBr beam splitter and DTGS KBr detector. A quest single reflection attenuated total reflectance (ATR) accessory was used for analysis in the mid and far infrared. 200 scans were collected in the 4000-500 cm⁻¹ spectral range at a resolution of 2 cm⁻¹.

2.3. Pozzolanic activity

Pozzolanic activity was assessed using the Frattini test, portlandite consumption test and strength activity index test. Finely ground quartz sand was tested at the same replacement levels as calcined clay to differentiate between pozzolanic and filler effects. The sand was ground identically to the calcined clay.

The Frattini test (BS EN 196-5:2011) used 20 g of test sample consisting of 80% CEM-I and 20% calcined clay (or sand) mixed with 100 ml deionised water in plastic vials. These were sealed and stored at 40°C for 8 and 15 days and vacuum filtered. The filtrate was analysed for [OH⁻] by titration against dilute HCl using methyl orange indicator, and [Ca²⁺] expressed as calcium oxide concentration [CaO] by titration against EDTA solution using Patton and Reeder's indicator (Donatello et al., 2010). These are calculated using the following equations according to BS EN 196-5:2011, in mmol/l:

$$[OH]^{-} = 2 \times V_3 \times f_2 \quad (1)$$

$$[CaO] = 0.6 \times V_4 \times f_1 \quad (2)$$

Where V_3 is the volume of 0.1 mol/l HCl solution used for titration in ml, f_2 is the factor of the HCl solution, V_4 is the volume of EDTA solution used for titration in ml and f_1 is the factor of the EDTA solution. [CaO] and [OH⁻] were compared with the solubility isotherm for calcium hydroxide at the same temperature. [CaO] and [OH⁻] below the solubility isotherm indicates that calcium hydroxide released during cement hydration is consumed and the calcined clay is pozzolanic.

The portlandite consumption test involved mixing 10 g of test material and 10 g of analytical grade Ca(OH)₂ with 20 ml of distilled water in plastic vials. The vials were sealed to prevent drying and samples were cured at 40°C for 3, 7, 14, 28 and 90 days. About 500 mg of the paste was extracted at different times and freeze-dried to inhibit hydration. TGA was then completed on the dried paste in a N₂

atmosphere to 1000°C at a heating rate of 10°C/min. The amount of Ca(OH)₂ in the paste was determined from the mass loss occurring at ~400-500°C. The mass loss at ~600-700°C due to decomposition of CaCO₃ was recorded to account for carbonation that inevitably occurs during sample preparation (Kim and Olek, 2012). The second derivative of the TGA curve was used to define the exact start and end temperature of decomposition. The amount of Ca(OH)₂ was calculated and expressed relative to the mass of test material as described by Kim and Olek (2012).

The strength activity index (SAI) is an indirect method of assessing pozzolanic activity from compressive strength data (ASTM C618-15; BS EN 450-1:2012). Control mortar samples were prepared by mixing 1350 g sand, 450 g CEM-I and 240 ml water and casting 50 mm cube samples. Test mortars were identically prepared, except 20% of CEM-I (90 g) was replaced by calcined clay (or silica sand). Mortar cubes were de-moulded after 24 hours and cured in a water bath at 23°C for 3, 7, 14, 28 and 90 days. The mortar samples were tested for compressive strength using three replicates in a universal testing machine and the SAI calculated from:

$$SAI = \frac{A}{B} \times 100\% \quad (3)$$

where A is the average compressive strength of the test mortar at a selected curing time (MPa) and B is the average compressive strength of control mortar at the same age (MPa). For a material to be pozzolanic the SAI must be >75% at 28 days (ASTM C618-15) or >75% at 28 days and >85% at 90 days according to BS EN 450-1 (2012).

2.4. Isothermal calorimetry

Isothermal calorimetry was used to investigate the influence of calcined clay on early age hydration (TAM Air Isothermal Calorimetry 8-channel, TA Instruments, USA). The rate of heat evolution (mW/g) and cumulative heat (J/g) of cement pastes containing 50% replacement of CEM I with either calcined London clay or sand was determined. Results were compared with control paste containing 100% CEM I. The w/b ratio for mixes was 0.5. Samples were prepared by hand mixing for 2 minutes and then ~10 g of paste was placed in the calorimeter vial and analysed for 48 hours. The operating temperature was 20 ± 0.02°C.

2.5. Preparation of concrete samples

a) Calcined clay

As-received London clay was formed into ~5 cm diameter balls, as shown in Fig. 1a. These were, oven dried at 110°C for 24 hours and calcined at the optimum calcining temperature (900°C) for 2 hours in a chamber furnace (Carbolite, UK). The calcined clay was ground to a fine powder using a vibratory disc mill (Gy-Ro, Glen Creston Ltd, UK) for 2 minutes. The median particle size and specific gravity of the calcined clay were 7.0 µm and 2.88 respectively.

Calcined clay is shown in Fig. 1b. This had a thin, ~4-5 mm, light brown/red surface layer and a black core (Fig. 1c). This effect is common in fired clay ceramics and is due to varying oxidation states of Fe across the sample (MacKenzie and Cardile, 1990). The dark core results from ferrous minerals, not present in the oxidized state near the surface, where Fe is present as Fe₂O₃. Ground calcined clay forms a dark brown powder, as shown in Fig. 1d.

b) Concrete samples

Concrete mix designs were calculated using the absolute volume method (Table 3) (Neville, 1996). This assumes the volume of compacted concrete is the sum of the absolute volumes of all components. Fifteen concrete mixes were prepared with different water/binder ratios (0.3, 0.4, and 0.5) with different levels of CEM I replaced by calcined clay (0, 10, 20 and 30%). An additional series of concrete mixes had a 0.4 water/binder ratio with 20% CEM I replaced by GGBS, PFA or SF. The total aggregate volume fraction in all mixes was 65% and the fine to coarse aggregate ratio was 0.35. Batch water was adjusted for aggregate absorption to ensure that identical free water/binder ratios were used.

Concrete samples were mixed using a 40-L pan and paddle driven mixer (Zyklos, Pemat, Germany). The coarse and fine aggregate and half of the water were mixed for 3 minutes. The cement containing dry-mixed SCMs and the remaining water were then added and intensively mixed for 3 minutes.

Concrete samples were cast to form 100 mm cubes in plastic moulds (Controls, UK), in 3 layers that were compacted using a vibrating table. Plastic moulds with expanded polystyrene board lids were used in preference to normal steel moulds because they provide increased heat insulation. Heat loss during initial curing in concrete samples containing pozzolans is reported to cause a decrease in strength

(Duran-Herrera et al., 2008). The polystyrene boards were used to cover samples to prevent evaporation and provide insulation. Samples were left for 24 hours and de-moulded using pressurised air before being cured at 23°C for 3, 7, 14 and 28 days in a water-bath.

2.6. Concrete testing

A standard slump test was performed on concrete mixes (BS EN 12350-2) to determine the slump value. Density was determined using a specific gravity balance (Stable Micro Systems, UK) and Archimedes' Principle. The compressive strength of surface dry 100 mm concrete cube samples was determined at 0.3 MPa/s (Automax 5, Instron, UK), in compliance with ASTM C39, using three replicate concrete cubes.

The efficiency factors of calcined London clay, GGBS, PFA and silica fume were determined to further assess the relative performance of the SCMs in concrete. The efficiency factor k was calculated from:

$$k = \frac{R_s m_{co} - m_c}{m_{SCM}} \quad (4)$$

where R_s is the relative strength (i.e. strength of concrete containing SCM divided by the strength of control concrete at the same age), m_{SCM} is the SCM content (kg/m³) in the blended mix, m_{co} and m_c are the cement content (kg/m³) in the control and blended mix respectively (Wong and Abdul Razak, 2005). A k factor of 1 indicates that the SCM has the same cementing efficiency as Portland cement, i.e. it can replace Portland cement on a weight-to-weight basis without affecting strength. Values of $k > 1$ indicate higher efficiency and conversely $k < 1$ indicates lower efficiency.

3. Results

3.1. Characterisation of raw and calcined London clay

The physical properties of as-received and ground calcined clays are summarised in Table 4. The particle size of as-received and calcined clays after grinding were fairly consistent, with values ranging from 0.6 to 1.6µm, 5 to 12µm and 32 to 55µm for d_{10} , d_{50} and d_{90} respectively. Thermal treatment did

not produce significant changes in the particle size distribution. The density of London clay increased with calcining due to loss of structural water. The BET surface area decreased as the calcining temperature increased from 600 to 1000°C due to agglomeration and sintering of clay particles (Alujas et al., 2015). Data for silica sand (after grinding) is also included in Table 4.

XRD data for as-received and calcined clay is shown in Fig. 2. Kaolinite, illite and smectite (montmorillonite) are the clay minerals in the as-received clay. This is consistent with the XRF data shown in Table 2, where the presence of K₂O is related to illite, while elevated Na₂O and MgO are associated to montmorillonite. XRD data shows a reduction of crystallinity and increasing amorphous phases in calcined samples. The peaks corresponding to kaolinite disappear at 600°C, indicating dehydroxylation. Peaks for illite and smectite decrease with increasing calcining temperature. These observations are consistent with other studies (Alujas et al., 2015; Fernandez et al., 2011). Formation of a γ -Al₂O₃ spinel phase is seen at 1000°C. The absence of mullite or cristobalite suggests recrystallization does not occur. Quartz, feldspar, hematite and goethite are present but show little change with thermal treatment. This suggests calcination temperatures of at least 900°C are required for complete dehydroxylation.

Fig. 3a shows thermogravimetric analysis data for the raw clay. The initial mass loss (region I) is due to evaporable water, surface adsorbed water and interlayer water. The significant mass loss occurring between 350-600°C (region II) is due to dehydroxylation of kaolinite and formation of metakaolin. The mass loss between 600°C and 950°C (region III) is attributed to dehydroxylation of 2:1 clay minerals such as illite and montmorillonite (smectites) (Alujas et al., 2015; Fernandez et al., 2011; He et al., 1995, 1996, 2000; Tironi et al., 2013). This is consistent with the XRD data. Fig. 3b shows the degree of dehydroxylation calculated from mass loss in the 350-950°C range. The degree of dehydroxylation is 69.7%, 80.1%, 89.1% and 98.5% at 600, 700, 800 and 900°C respectively. Therefore, the dehydroxylation of 2:1 clay minerals represents a substantial fraction (~30%) of the total dehydroxylation. Given that the theoretical mass loss from complete dehydroxylation is 13.9% for pure kaolinite on a dry weight basis and 5% for illite and montmorillonite (Earnest, 1988; Todor, 1976), it is estimated that London clay contains ~26 wt.% kaolinite and 32 wt.% illite and montmorillonite. This

assumes that complete dehydroxylation has occurred, that no other components contribute to weight loss and there is no overlap in decomposition temperatures of the clay minerals.

FTIR absorption spectra are shown in Fig. 4. The spectrum for raw clay exhibits several characteristic bands corresponding to stretching vibrations of O-H bonds ($3697, 3620\text{ cm}^{-1}$), Al-OH (912 cm^{-1}), Si-O (1117 cm^{-1}), Si-O-Al_{IV} (752 cm^{-1}) and Si-O-Al_{VI} ($\sim 523\text{ cm}^{-1}$) (Madejova, 2003; Russel, 1987; Wilson, 1994). Several changes to the FTIR spectra are noted for calcined clays. In particular, the absence of absorption bands at $3697, 912$ and 532 cm^{-1} at 600°C show dehydroxylation of kaolinite, in agreement with XRD data. The intensities of bands at $3620, 1117$ and 752 cm^{-1} gradually decrease with increasing temperature, disappearing at 900°C . This is due to dehydroxylation of illite and montmorillonite. The bands at 3400 and 1637 cm^{-1} are due to OH stretching and deformation of water molecules and these diminish with increasing temperature. In contrast, the absorption bands at $1162, 796, 778$ and 694 cm^{-1} are the Si-O stretching frequencies of quartz. These are unaffected as quartz is stable within this temperature range. The band at $\sim 993\text{ cm}^{-1}$ representing the peak of in-plane Si-O stretching shifts slightly to higher wave number as temperature increases. This results from formation of a three-dimensional amorphous silica framework (Madejova, 2003).

3.2. Effect of calcination temperature on pozzolanicity

Frattini test data in Fig 5 shows $[\text{CaO}]$, equivalent to $[\text{Ca}^{2+}]$, in mmol.l^{-1} on the y-axis, and $[\text{OH}^-]$ in mmol.l^{-1} on the x-axis. The solubility curve of lime at 40°C is included to interpret titration data. Samples containing silica sand and clay calcined at 600°C and 700°C are above the solubility curve after 8 and 15 days and these do not show significant pozzolanic reactivity. The samples containing clay calcined at 800°C , 900°C and 1000°C are below the curve after 8 and 15 days and this indicates calcium hydroxide released during hydration has been consumed and therefore these materials are pozzolanic. Although calcination at 600 and 700°C does not produce pozzolanicity, the results at 15 days are closer to the lime solubility curve than at 8 days, indicating that calcium hydroxide is consumed by reaction with these calcined clay samples. Similarly, the Frattini test results at 15 days for clay calcined at $800, 900$ and 1000°C fall further below the solubility curve than the 8 day results, indicating continued pozzolanic reaction with curing time.

Fig. 6a shows typical TGA data from the portlandite consumption test after 28 days. All samples showed major losses at temperatures between ~400-500°C (region I) and ~600-800°C (region II), due to dehydroxylation of Ca(OH)_2 and decarbonation of CaCO_3 respectively. The amount of Ca(OH)_2 decomposition in mixes containing calcined clay is lower compared to the mix containing silica sand (filler), presumably as a result of pozzolanic reaction. Furthermore, mixes containing calcined clay show additional mass loss, particularly at temperatures <400°C. These are not significant in the mix containing silica sand and are associated with dehydroxylation of the hydration products (e.g. C-S-H, C-A-H and C-A-S-H phases) formed from the reaction between calcined clay and portlandite.

Fig. 6b shows the Ca(OH)_2 consumed per mass of test material, calculated from TGA data. Samples containing sand (filler) showed very little portlandite consumption at all ages. Samples containing calcined clay showed significant portlandite consumption from early ages that increased with curing. Clay activated at 800 and 900°C gave the highest reactivity, followed by 1000°C, 700°C and 600°C. The portlandite consumed was relatively constant after 28 days. The mixes contained excess portlandite and this suggests that nearly all the calcined clay minerals have reacted by the end of the experiment. In the most reactive samples (800°C and 900°C), the maximum amount of Ca(OH)_2 consumed was ~0.71 g/g of calcined London clay. Stoichiometric calculations show that complete pozzolanic reaction of 1g of calcined kaolin (or montmorillonite) consumes ~1g of Ca(OH)_2 (He et al., 1994; Murat, 1983). If all calcined clay minerals are assumed to have fully reacted by the end of the experiment, these results imply that calcined London clay contains about 30wt. % of non-reacting impurities. There is a possibility that the reaction is not complete and that a small amount of pozzolanic material or less reactive phases remain, and therefore this estimation represents an upper limit.

SAI test data for mortar cubes tested after curing for 3, 7, 14 and 28 days are given in Fig. 7 with error bars indicating +/- one standard error. All test mortars containing calcined clay had similar strengths at 3-days, except the one with clay calcined at 1000°C which had lower strength. All other samples gained less than 80% of the strength of the control mortar due to the dilution effect. Similar results were obtained at 7 days, but by 14 and 28 days the strengths of the mortars containing calcined clay were similar but slightly below the strength of control samples, with 900°C calcined clay having

the highest strengths. Results at 90 days show that mortars containing clay calcined at 800, 900 and 1000°C have similar strengths to control samples, with the 900°C calcined clay giving the highest strength concrete. Clays calcined at 600 and 700°C show low pozzolanic activity in the SAI test, in agreement with the Frattini and portlandite consumption tests.

The SAI of mortar cubes containing London clay calcined at 700-1000°C were all greater than 0.75 at 28-day and 0.85 at 90-day. 900°C was the most effective calcining temperature and subsequent concrete testing experiments used London clay calcined at this temperature. Mortar samples containing sand had comparable strengths to the samples containing calcined clays up to 14 days, but failed to meet the ASTM C618-15 and EN 450-1 SAI requirements for pozzolanicity at 28 and 90-day.

3.3. Isothermal calorimetry

Fig. 8 shows rate of heat evolution and cumulative heat during the first 48 hours of hydration. Results are normalised to the mass of binder (CEM I and replacement material). The rate of heat evolution shows a high initial peak within the first few minutes due to dissolution of cement and initial formation of ettringite. A short induction period follows before the reaction rate increases, producing a well-defined second peak at ~10 hours, corresponding to C₃S hydration. A third peak is sometimes observed several hours later, related to renewed reaction of C₃A to form ettringite following exhaustion of gypsum (Hewlett, 2003; Taylor, 1997).

At very early age (<5-10 hours), pastes containing clay calcined at 600°C showed the highest rate of heat evolution and total heat released, followed by the 700°C, 800°C and the control paste. Pastes containing clay calcined at 900 and 1000°C, and sand gave lower rates and cumulative heats compared to the control. After 48 hours all blended mixes released significantly lower heat than the control. This is because they contained lower CEM I content, i.e. the dilution effect, consistent with the low early age strengths observed in the SAI test (Fig. 7). The magnitude of heat reduction is less than expected from the proportion of cement replaced (50%). For example, the total heat released for pastes containing clay calcined at 600, 700 and 800°C were on average only 23% below the control. Samples containing clay calcined at 900 and 1000°C and silica sand released on average 41.5% lower heat than the control.

These observations suggest that finely divided calcined clay and silica sand act as fillers and provide additional nucleation sites that accelerate CEM I hydration. Fillers with greater surface area have a greater accelerating effect and these trends are consistent with the specific surface data shown in Table 4. The specific surface was highest for clay calcined at 600°C, and decreased with increasing calcining temperature due to sintering and agglomeration effects. The sand had similar specific surface area to the 1000°C calcined clay. Considering the specific surface of CEM I is typically ~300-400 m²/kg, calcined clay is around 5-60 times finer than CEM I. Another interesting observation is the appearance of a third peak in the rate of heat evolution for pastes containing calcined clay. This suggests an additional exothermic reaction is occurring and the possibility that C₃A hydration is accelerated in the presence of calcined clay.

3.4. Workability and strength of concrete containing London clay calcined at 900°C

Slump test results are shown in Fig. 9a. As expected, slump decreased with decrease in w/b ratio. However, replacing CEM I with calcined London clay did not produce a consistent or significant effect on slump. Visual inspection also found that inclusion of calcined clay had no appreciable effect on bleeding and segregation.

The effect of 20 wt.% cement replacement using SCMs (PFA, GGBS, SF) on slump was compared to calcined London clay at w/b of 0.4. The slump values of concrete containing PFA and GGBS were 90 mm and 80 mm respectively. These were higher than the control sample (60 mm) and sample containing calcined London clay (45 mm). Concrete containing SF had zero slump. The results show that, as expected, replacing CEM I with SCM of very high surface area such as silica fume (see Table 4) at constant w/b ratio has a negative effect on workability.

The densities of concrete samples containing calcined clay are shown in Fig. 9b. Concrete mixes with lower w/b ratio had higher densities and for a given w/b ratio higher calcined clay content reduced the density.

Compressive strength data of samples containing calcined London clay tested at 3, 7, 14, 28 and 90 days is shown in Fig. 10. Samples with w/b ratio of 0.3 had the highest compressive strengths at all ages, followed by w/b 0.4 and 0.5. Concrete samples containing calcined London clay had reduced

strength at 3 and 7-days compared to control mixes and samples with higher calcined clay content had lower strength, consistent with dilution effects and pozzolanic reactivity (Fig. 6b). Strength differences reduce with curing age. 7 day samples containing calcined clay gained strength at a greater rate than the control. Strength development continues beyond 28 days and this suggests that later age pozzolanic reactions, most likely from calcined montmorillonite (Fernandez et al., 2011) have a considerable effect.

The improvement in strength of samples containing calcined clay was most pronounced at a w/b ratio of 0.3 (Fig. 10c). All samples containing calcined clay had greater strength after 28 days compared to control samples. For concretes with w/b of 0.4, samples containing calcined clay achieved 90-day strengths equivalent to, or greater than, the control. The best performing mixes had strengths about 10% greater than control samples and the optimum cement replacement by calcined clay was 20%.

Results in Fig. 11 show that strength efficiency factor increases with curing age due to the increase in relative strength from pozzolanic reactions. At 90 days, the calcined clay in concretes with a w/b ratio of 0.3 and 0.4 have efficiency factors greater than 1, with values up to 1.8 observed. Concrete samples with w/b 0.3 had the highest values. Fig. 11d shows that the efficiency factor for calcined London clay is comparable to silica fume at all ages. The efficiency factors for GGBS and PFA are low at early ages, but achieve similar values to calcined clay and silica fume after 90 days, reflecting the relatively low reactivity of GGBS and PFA at early age.

4. Discussion

The London clay sample used contained kaolinite, illite, smectite, quartz, feldspar, goethite and hematite. London clay mineralogy varies and it may contain quartz (20-70%), feldspar (albite, K-feldspar, <10%) phyllosilicates/clay minerals (40-80%), carbonate minerals (calcite, dolomite, siderite, generally < 3%, together with traces of pyrite, goethite and gypsum (Kemp and Wagner, 2006). Clay content is greater towards the east of London, containing proportionally more smectite clays, with clay mineral fractions reported to be 44-46% smectite, 35-40% Illite, 11-12% kaolinite and 5-7% chlorite (Huggett and Knox, 2006). London clay may also contain carbonate concretions (cementstone nodules and septarian nodules), disseminated pyrite, and numerous plant and animal fossils.

Thermal treatment of clays has been extensively studied (MacKenzie, 1966). Calcination causes adsorbed moisture to evaporate, re-alignment of clay platelets and structural collapse of mineral bearing water at interlayer sites. Above $\sim 600^{\circ}\text{C}$ structural water is removed, as hydroxyl ions combine to form water in the gas phase, leaving oxygen ions to re-combine with the solid, resulting in structural changes to the lattice. At higher temperatures, ion mobility causes the solids to re-order. If heating continues the minerals partially melt, promoting sintering and forming clay ceramics. Maximum pozzolanic activity occurs when the structure is fully dehydrated and partially disordered, but has neither the time nor energy to re-form into a more ordered, stable state (He et al., 1995, 1995b, 1996, 2000). Kaolinite becomes reactive around 650°C , smectite group clays at or above $\sim 830^{\circ}\text{C}$ and illite at $\sim 930^{\circ}\text{C}$.

The production of pozzolans from natural clays should be optimized by experiment, as the mineral content varies with location. Screening of calcined clays by the Frattini test, portlandite consumption test and strength activity index test is robust and reliable. These tests show the reactivity of London clay increases with calcining temperature due to more complete thermal activation of the clay minerals, with $800\text{--}900^{\circ}\text{C}$ giving the highest pozzolanic activity. This is supported by XRD and FTIR data showing a more disordered structure and TGA data showing more complete dehydroxylation in this temperature range. The optimum temperature is consistent with previous studies, indicating that 2:1 clay minerals such as smectites and illites require higher calcination temperatures for complete dehydroxylation compared to kaolinites (Fernandez et al., 2011; He et al., 1995, 1995b, 1996, 2000). The decrease in specific surface area above 800°C does not have a significant effect on pozzolanic activity (Alujas et al., 2015).

When calcined clay partially replaces Portland cement in concrete several effects occur. The dilution effect from reduced cement content and increased w/c ratio has a negative impact on strength development. However, finely divided clay minerals, quartz and other impurities act as fillers and provide nucleation sites that accelerate cement hydration. The pozzolanic reactions form additional products causing densification and improved mechanical properties. For metakaolin, the main products are C-S-H, C_2ASH_8 (stratlingite) and some C_4AH_{13} and C_3ASH_6 (siliceous hydrogarnet) (Cabrera and Rojas, 2001; Murat, 1983; Pera and Amrouz, 1998; Wild et al., 1996). Calcined montmorillonite produces C-S-H as the main product (Hewlett, 2003). Pozzolanic reactivity depends on the type and

quantity of clay minerals, impurities, thermal activation conditions (temperature, residence time), amorphous phase content, particle size and specific surface area after calcination (Ambroise et al., 1985; Murat, 1983; Shvarzman et al., 2003; Tironi et al., 2013). Kaolinite has the highest pozzolanic activity due more hydroxyl groups and greater disorder during dehydroxylation (Alujas et al., 2015). Montmorillonite and illite exhibit lower pozzolanic reactivity, despite higher activation temperatures (Ambroise et al., 1985b; Fernandez et al., 2011; He et al., 1995, 2000). Pozzolanic reactivity is also dependent on cement composition, the level of replacement, w/b ratio, curing time and temperature.

The replacement of 30% of Portland cement (CEM I) by London clay calcined at 900°C has little effect on concrete workability or compressive strength. Concrete containing calcined London clay achieves strengths that exceed control mixes after 28-days. London clay it can be processed into an effective SCM despite relatively low kaolinite content. The additional hydration products formed and strength contribution due to pozzolanic reactions compensates for the dilution effect.

Pozzolanic reactions are limited by the availability of Ca(OH)_2 . On complete hydration, the amount of Ca(OH)_2 liberated is typically 15-25 wt. % of the reacted cement, depending on the C_3S and C_2S content (Taylor, 1997). CEM I produces ~ 0.2 g Ca(OH)_2 per g of reacted cement (Lothenbach and Winnefeld, 2006) and the portlandite consumption test shows 1g of calcined clay consumed ~ 0.71 g Ca(OH)_2 on complete reaction of reactive samples (800-900°C). The ideal combination to ensure complete reaction of calcined clay and depletion of Ca(OH)_2 would be 0.28 g calcined clay per g CEM I. This is a 78: 22 CEM I: calcined London clay wt.% blend. This agrees with the experimental results which show a replacement level of 20% was optimum for strength. Higher replacement levels ensure complete Ca(OH)_2 depletion, but produce greater cement dilution, higher impurities (quartz, feldspar etc) and residual unreacted clay minerals.

Over the last 25 years the cement industry has made significant progress to improve process efficiency and reduce carbon emissions (WBCSD, 2002). Developments in low-energy clinkers, new and improved pozzolans and clinker production have reduced the overall energy associated with cement and concrete. Potential ways to reduce CO_2 emissions from cement have been reviewed (Damtoft et al., 2008). A modern plant uses ~ 3.06 GJ per tonne of Portland cement clinker and use of SCMs has

significant potential to deliver further CO₂ reduction. Blending SCMs with clinker offers great potential for reducing the embodied CO₂ of concrete.

The two materials that dominate the SCM market are pulverised fuel ash (PFA) and ground granulated blast furnace slag (GGBS). If all suitable, but currently unused PFA and GGBS were blended with cement clinker (1:1 wt./wt.) the corresponding reduction in CO₂ would be ~17% (Damtoft et al., 2008). These materials and silica fume are by-products of energy-intensive processes and the long-term supply will diminish. The global demand to reduce reliance on fossil fuel for energy production may reduce the supply of PFA and while global demand for steel is unlikely to diminish, production in Europe will decrease, with associated reduction in the availability of GGBS and SF (Worrell et al., 2001). Demand for alternative pozzolans will increase and calcined clays have wide availability and low calcination temperatures that can be achieved using biofuels. Increased use of SCMs will reduce greenhouse gas emissions, but the location of SCMs is often remote from potential markets, limiting economic re-use. This is not true for clays which are widely available.

Why have calcined clays not been more widely used? Although there is provision for using calcined clays in cement standards, the materials vary in composition and they are not currently commercially available. The wide availability of the raw material, combined with increasingly stringent controls on CO₂ emissions, may force a step-change in the cement industry. The global move from exclusive, composition-based standards, to inclusive, performance based standards will help this happen.

Developing nations are experiencing rapid urbanization, population increase and increasing demand for affordable housing. Meeting this demand and the obligation to minimize CO₂ emissions means that the use of SCMs is critically important.

The use of calcined clay in concrete has significant energy and carbon savings. A preliminary assessment can be obtained by considering carbon emissions. The specific heat capacity of London clay is ~900 J/kgK (Doty and Turner, 2012). The energy required to heat one tonne of London clay to 900°C from 100°C is therefore:

$$\begin{aligned} E &= m \times c \times \Delta T \\ &= 1000 \times 900 \times (900 - 100) = 720 \text{ MJ} = 200 \text{ kWh} \end{aligned} \tag{4}$$

where E is the energy, m is the mass, c is the specific heat capacity and ΔT is the change in temperature. 900°C can be achieved by the combustion of biomass rather than fossil fuels (Palmer et al., 2011). The carbon emissions of biomass combustion is 0.35 kgCO₂/kWh (Defra and DECC, 2012) and therefore the emissions associated with the production of one tonne of calcined London clay is:

$$200 \text{ kWh} \times 0.35 \text{ kgCO}_2/\text{kWh} = 70 \text{ kgCO}_2$$

The carbon emissions associated with calcining London clay is therefore ~70 kgCO₂/tonne which is ~91% less than CEM I, assuming production of one tonne of Portland cement clinker emits ~800 kgCO₂. A 20 wt.% replacement of cement in concrete by calcined London clay therefore reduces carbon emissions from 800 kgCO₂/tonne for 100% CEM I, to 650 kgCO₂/tonne for an 80:20 CEM I:calcined London clay binder, equivalent to an 18% reduction overall. At 30 wt.% replacement carbon emissions are reduced by 27%.

The carbon emissions associated with calcined London clay are comparable to the 67 kgCO₂/tonne reported for GGBS (CSMA, 2010). The energy required for drying and grinding has not been considered but there would be additional energy savings from using heat recovery technologies.

This research therefore indicates the potential for developing a new circular economy industry using excavated clay mineral wastes from infrastructure development projects as the raw material to manufacture technically and commercially viable SCMs. London clay can be calcined at 800-900°C to produce a pozzolanic SCM with properties and performance comparable to PFA, GGBS and silica fume.

5. Conclusions

London clay is available in significant quantities from major infrastructure projects involving excavation and tunneling. Excavated London clay can be transformed into a pozzolanic SCM by calcining at 800-900°C. This temperature can readily be achieved using low-carbon biomass fuels. Replacing CEM I with 30% London clay calcined at 900 °C had no detrimental effects on workability or long-term (90 days) compressive strengths. Concretes at w/b 0.3 containing calcined London clay achieved strengths exceeding that of the CEM I control concrete at 28 days. Calcined London clay has similar performance to PFA, GGBS and SF in concrete. The carbon emissions producing calcined London clay are

significantly lower than those associated with manufacturing Portland cement (CEM I). A 20-30wt. % replacement of CEM I by calcined London clay produces a cementitious binder with 18-27% lower carbon emissions. Further research is required to quantify the long-term durability of concrete containing calcined London clay and the commercial viability of producing SCMs from excavated London clay needs to be further assessed.

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Table 1

Particle size distribution of fine and coarse aggregate.

| Sieve (mm) | Percentage passing (%) | | | | | | | | |
|------------|------------------------|------|------|------|------|------|------|-----|-----|
| | 0.075 | 0.15 | 0.3 | 0.6 | 1.25 | 2.5 | 5 | 10 | 14 |
| Fine | 0.3 | 3.2 | 19.4 | 58.5 | 76.9 | 87.3 | 99.4 | 100 | 100 |
| Coarse | 0.05 | 0.1 | 2.1 | 4.5 | 7 | 9 | 11 | 92 | 100 |

Table 2

XRF composition analysis data expressed as oxides for CEM I, as-received London clay, GGBS, PFA and silica fume.

| Oxides | CEM I (%) | As-received London clay (%) | GGBS (%) | PFA (%) | Silica fume (%) |
|--------------------------------|-----------|-----------------------------|----------|---------|-----------------|
| SiO ₂ | 21.0 | 45.8 | 31.8 | 54.8 | 94.0 |
| Al ₂ O ₃ | 4.4 | 12.8 | 10.8 | 21.3 | - |
| Fe ₂ O ₃ | 2.7 | 7.7 | 0.3 | 12.1 | 1.0 |
| K ₂ O | 1.4 | 3.7 | 1.0 | 3.0 | 1.6 |
| MgO | 1.6 | 1.8 | 17.2 | - | 2.5 |
| CaO | 64.7 | 1.1 | 35.4 | 4.3 | 0.2 |
| TiO ₂ | - | 1.2 | 0.4 | 1.1 | - |
| SO ₃ | 3.1 | 1.3 | 2.7 | 2.1 | 0.7 |
| Na ₂ O | 0.6 | 0.9 | - | - | - |
| P ₂ O ₃ | - | 0.1 | - | - | - |

Table 3

Mix proportions of all concrete mixes prepared in this study.

| Mix | w/b ratio | Water (kg/m ³) | CEM I (kg/m ³) | SC M (%) | SCM (kg/m ³) | | | | Fine aggregate (kg/m ³) | Coarse aggregate (kg/m ³) |
|-----------|-----------|----------------------------|----------------------------|----------|--------------------------|------|------|-------|-------------------------------------|---------------------------------------|
| | | | | | CLC * | PFA | SF | GGB S | | |
| Series I | | | | | | | | | | |
| 1 | 0.5 | 208.0 | 415.9 | 0 | - | - | - | - | 562.8 | 1045.1 |
| 2 | 0.5 | 208.0 | 374.3 | 10 | 41.6 | - | - | - | 559.8 | 1045.1 |
| 3 | 0.5 | 208.0 | 332.7 | 20 | 83.2 | - | - | - | 556.9 | 1045.1 |
| 4 | 0.5 | 208.0 | 291.2 | 30 | 124.8 | - | - | - | 554.0 | 1045.1 |
| 5 | 0.4 | 189.6 | 473.9 | 0 | - | - | - | - | 562.8 | 1045.1 |
| 6 | 0.4 | 189.6 | 426.5 | 10 | 47.4 | - | - | - | 559.4 | 1045.1 |
| 7 | 0.4 | 189.6 | 379.1 | 20 | 94.8 | - | - | - | 556.1 | 1045.1 |
| 8 | 0.4 | 189.6 | 331.7 | 30 | 142.2 | - | - | - | 552.7 | 1045.1 |
| 9 | 0.3 | 165.2 | 550.6 | 0 | - | - | - | - | 562.8 | 1045.1 |
| 10 | 0.3 | 165.2 | 495.6 | 10 | 55.1 | - | - | - | 558.9 | 1045.1 |
| 11 | 0.3 | 165.2 | 440.5 | 20 | 110.1 | - | - | - | 555.0 | 1045.1 |
| 12 | 0.3 | 165.2 | 385.5 | 30 | 165.2 | - | - | - | 551.1 | 1045.1 |
| Series II | | | | | | | | | | |
| 13 | 0.4 | 189.6 | 379.1 | 20 | - | 94.8 | - | - | 539.8 | 1045.1 |
| 14 | 0.4 | 189.6 | 379.1 | 20 | - | - | 94.8 | - | 537.7 | 1045.1 |
| 15 | 0.4 | 189.6 | 379.1 | 20 | - | - | - | 94.8 | 560.5 | 1045.1 |

* CLC = Calcined London Clay (900°C)

Table 4

Physical properties of raw and calcined London clay, silica sand after milling, GGBS, PFA and silica fume.

| Materials | d ₁₀ (μm) | d ₅₀ (μm) | d ₉₀ (μm) | Absolute density (g/cm ³) | BET surface area (m ² /g) |
|----------------------|----------------------|----------------------|----------------------|---------------------------------------|--------------------------------------|
| As-received clay | 1.6 | 9.0 | 49.8 | 2.6 | 45.1 |
| 600°C calcined | 1.1 | 8.2 | 32.4 | 2.8 | 18.5 |
| 700°C calcined | 1.2 | 11.5 | 55.4 | 2.8 | 16.9 |
| 800°C calcined | 1.1 | 10.4 | 55.4 | 2.8 | 13.7 |
| 900°C calcined | 0.8 | 7.0 | 44.7 | 2.9 | 5.6 |
| 1000°C calcined | 0.8 | 5.1 | 32.4 | 2.7 | 2.2 |
| Silica sand (milled) | 1.4 | 21.6 | 145.5 | 2.7 | 2.1 |
| GGBS | 1.6 | 16.1 | 81.3 | 3.1 | 1.5 |

| | | | | | |
|-------------|-----|------|------|-----|------|
| PFA | 1.9 | 15.3 | 72.1 | 2.4 | 2.7 |
| Silica fume | 0.9 | 6.9 | 18.8 | 2.4 | 25.1 |

Table 5

Compressive strength of concretes with a w/b = 0.4 and 20 wt.% replacement of CEM I with London clay calcined at 900°C, GGBFS, PFA and SF. Standard deviations are shown in brackets.

| Curing time (days) | Compressive strength (MPa) | | | | |
|-----------------------|----------------------------|-------------------------|-------------|-------------|-------------|
| | Control | Calcined London clay | GGBFS | PFA | SF |
| 3 | 42.3 (0.39) | 36.9 (1.44) | 36.6 (1.19) | 33.4 (0.28) | 37.6 (1.47) |
| 7 | 48.5 (0.99) | 44.7 (0.19) | 45.1 (0.92) | 38.9 (0.07) | 46.5 (0.57) |
| 14 | 54.0 (0.34) | 50.7 (0.61) | 50.5 (0.79) | 46.2 (0.80) | 51.9 (0.48) |
| 28 | 56.4 (0.12) | 58.0 (0.76) | 55.5 (0.81) | 49.8 (0.30) | 57.8 (0.65) |
| 90 | 58.8 (2.45) | 63.0 (1.96) | 62.3 (1.06) | 63.0 (1.07) | 61.5 (1.05) |



(a)



(b)



(c)



(d)

Fig. 1. Preparation of calcined London clay: a) moist clay shaped into small balls ready to be oven-dried; b) calcined London clay balls showing an orange coloured surface; c) cross-section of the calcined clay showing a brown core; d) calcined London clay in powder form after milling.

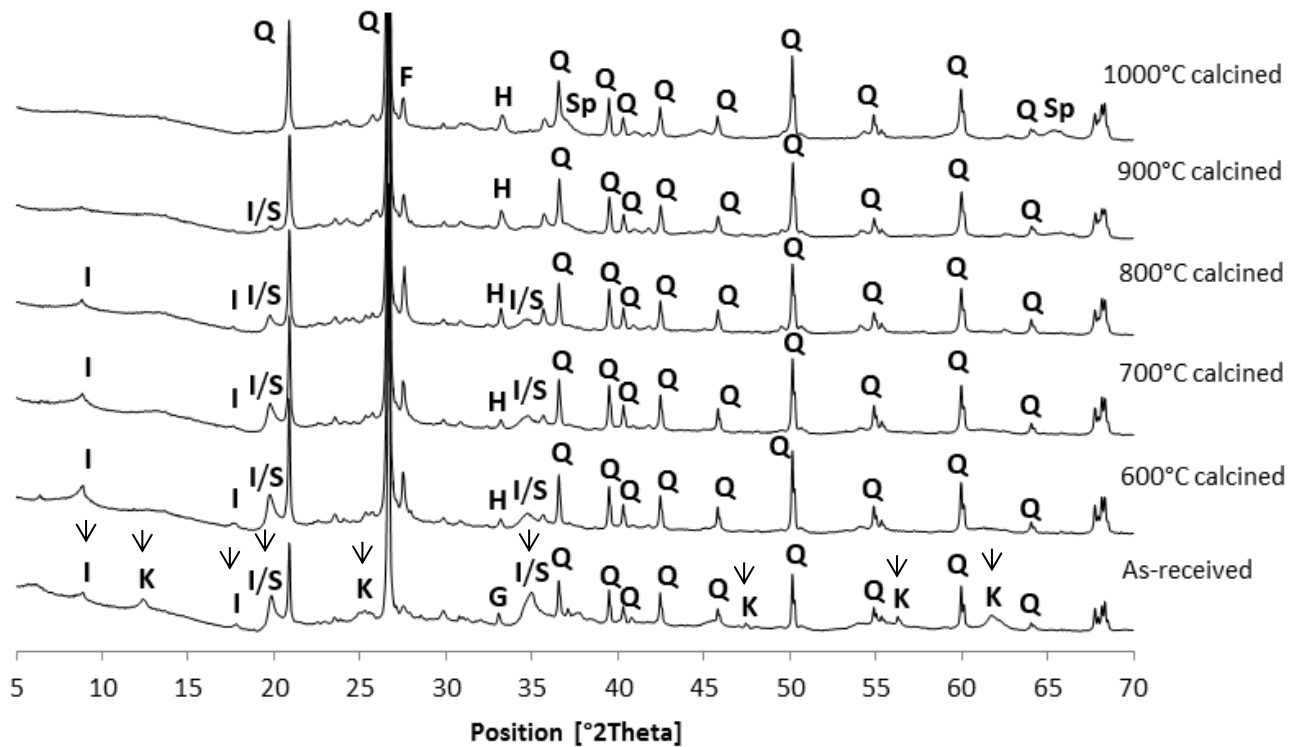
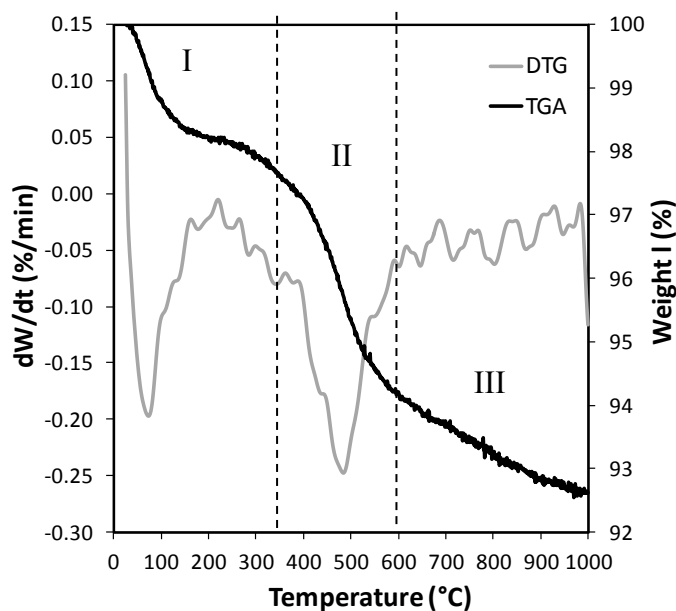
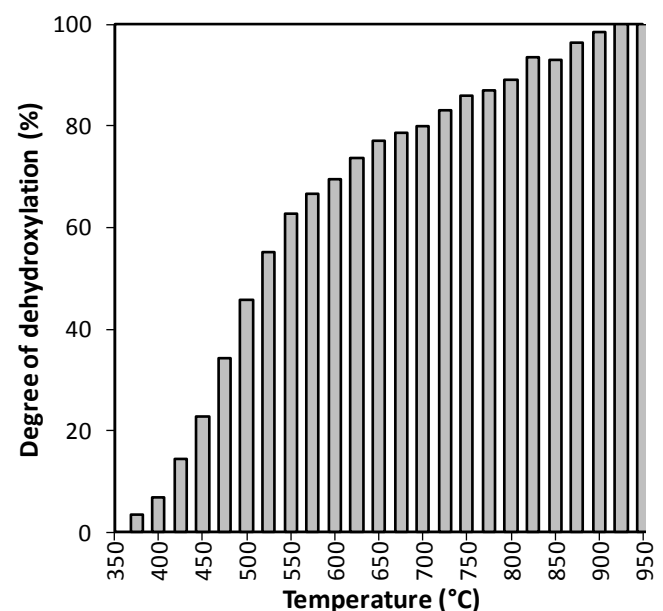


Fig. 2. XRD data of as-received London clay and London clay calcined at different temperatures (K: Kaolinite; I: Illite; S: Smectite; Q: Quartz; F: Feldspar; H: Hematite; G: Goethite; Sp: Spinel).

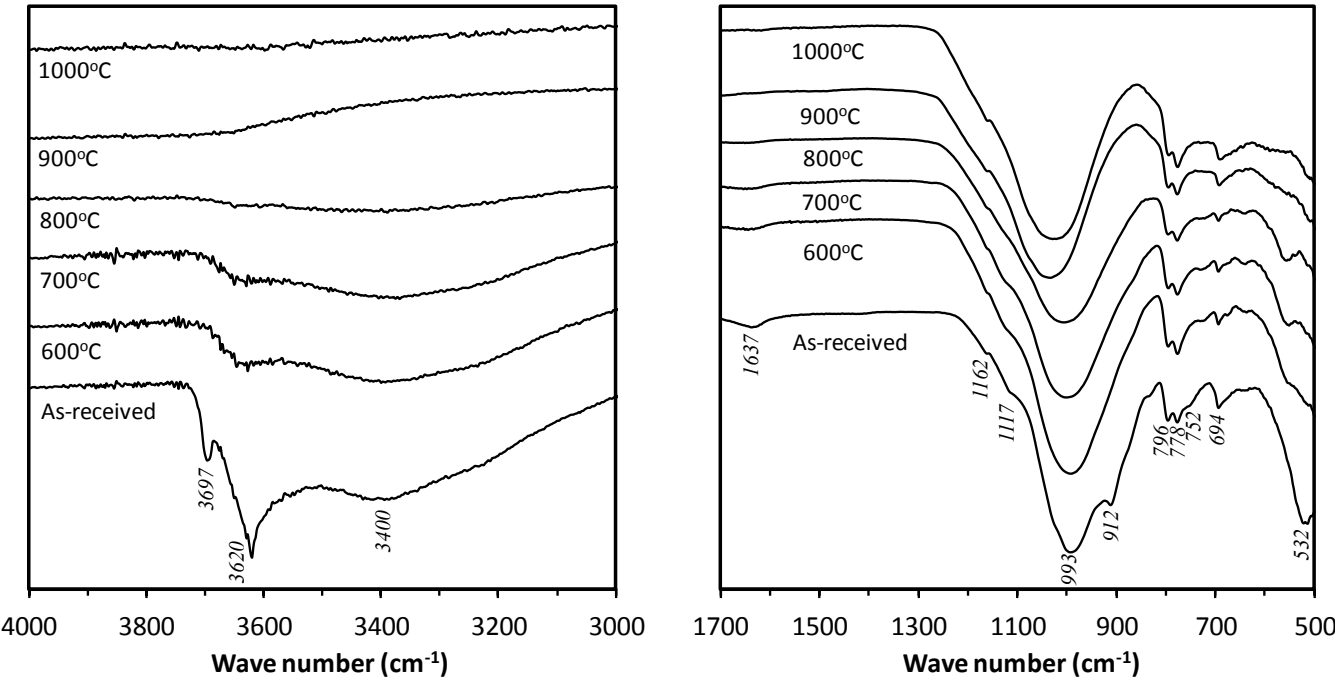


a) TGA/DTG

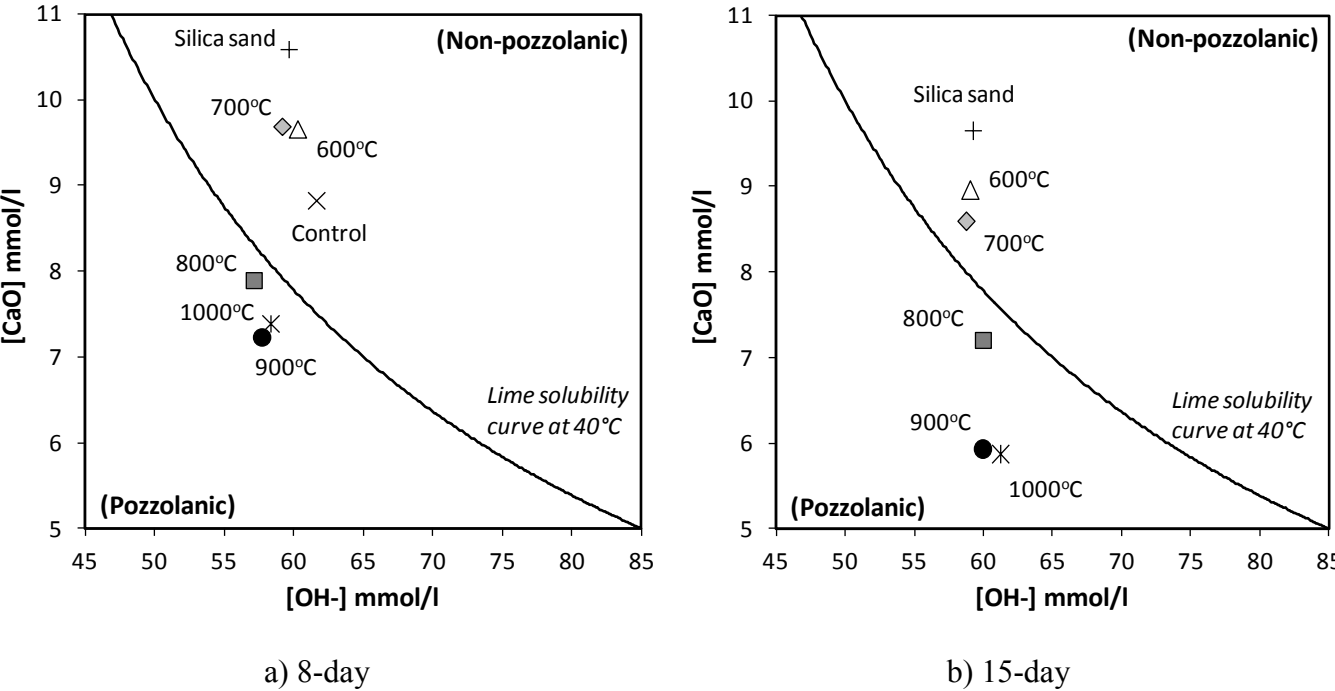


b) Dehydroxylation degree

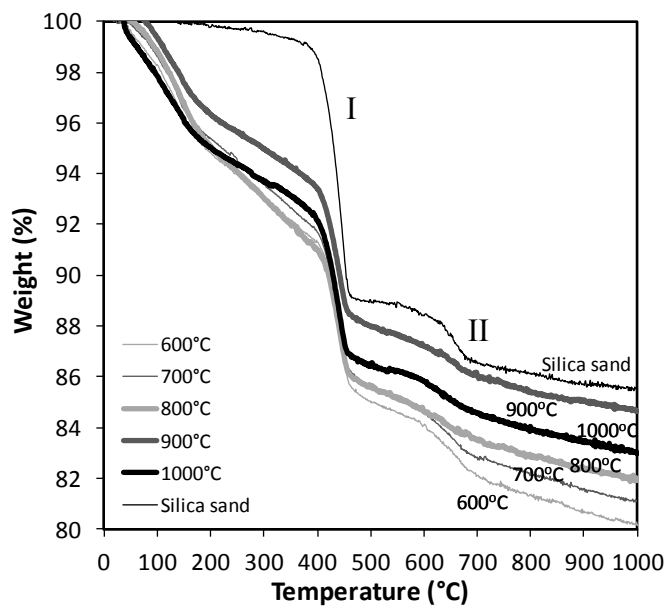
Fig. 3. Thermogravimetric analysis of the as-received London clay and the effect of calcining temperature on the degree of dehydroxylation.



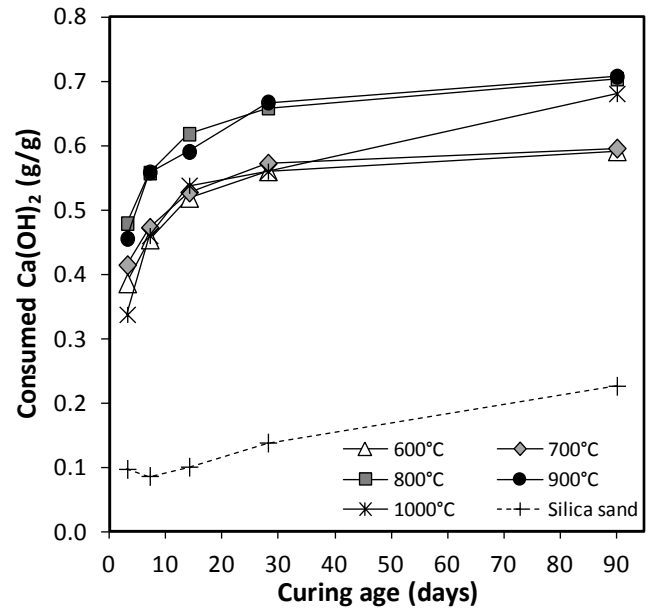
696 **Fig. 4.** FTIR absorption spectra of the raw and calcined London clay
697



698 **Fig. 5.** Frattini test results after 8 and 15 days of curing at 40°C for blended cements
699 containing 20% London clay calcined at various temperatures. Solid line shows the solubility
700 curve of lime (CaO) at 40 °C.
701



a) TGA data at 28-day



b) Portlandite consumption

Fig. 6. a) Thermogravimetric analysis of portlandite-calcined London clay mixtures after 28-day curing, and b) calculated portlandite consumption, in g/g of binder, at various curing ages.

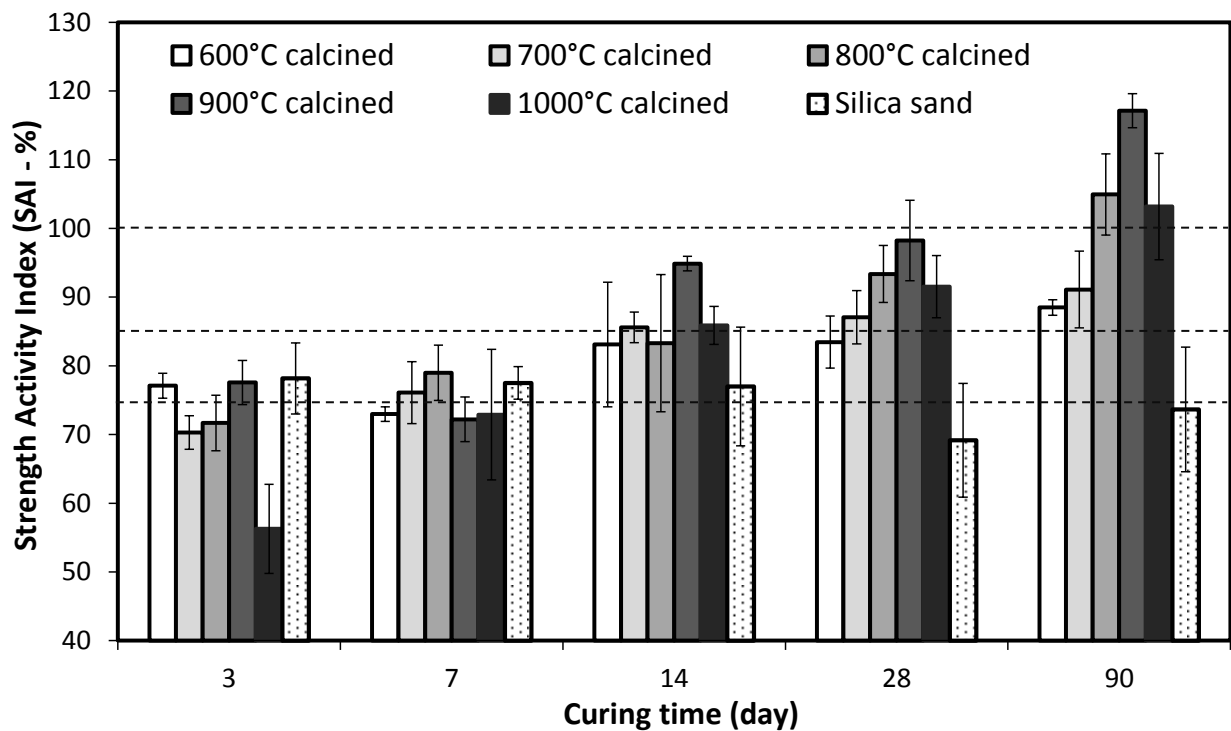
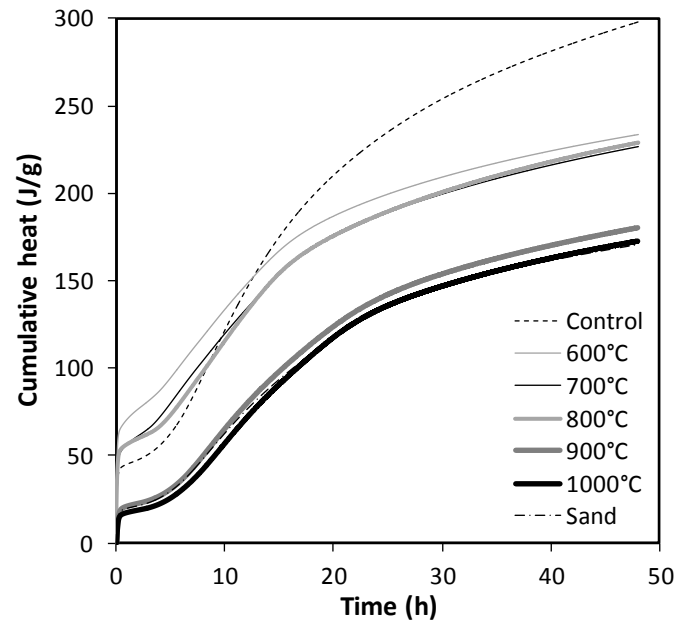
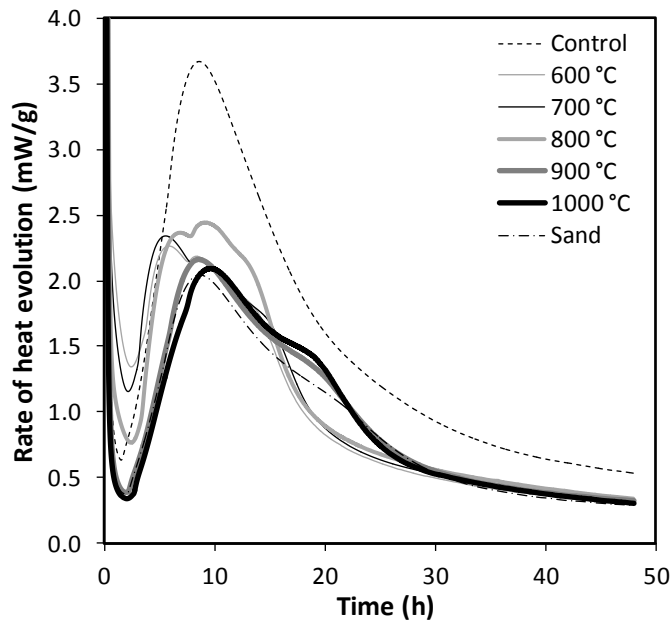


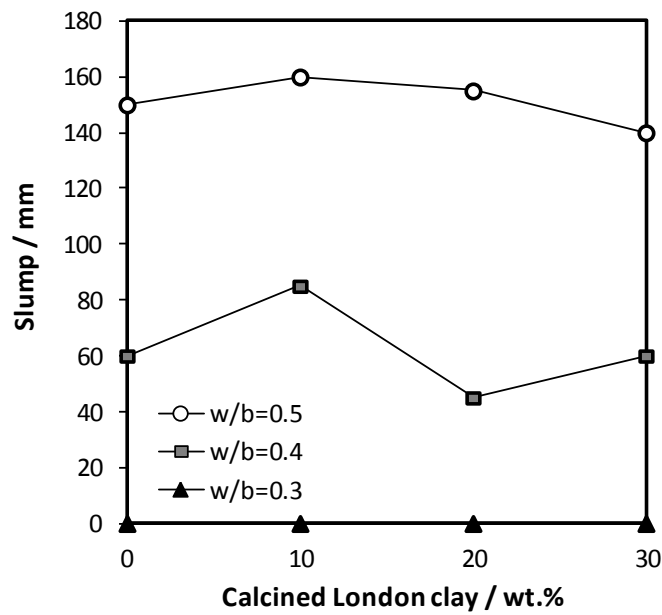
Fig. 7. Strength activity index (SAI) test data showing the development of compressive strength for control mortar cubes and test mortar cubes containing 20% calcined London clay. The data for silica sand (milled) demonstrates that the strengths gained with calcined clays are not due to a simple filler effect.



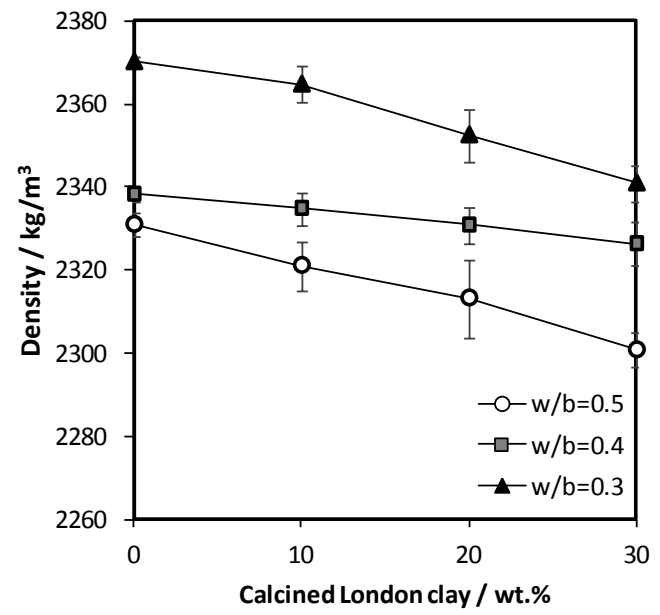
a)

b)

Fig. 8. Isothermal conduction calorimetry of cement pastes to evaluate the effect of calcined clay on a) rate of heat evolution, and b) cumulative heat of hydration.



a)



b)

Fig. 9. Effect of calcined London clay (900 °C) on the a) slump of fresh concrete and b) density of hardened concrete at several cement replacement levels and w/b ratios.

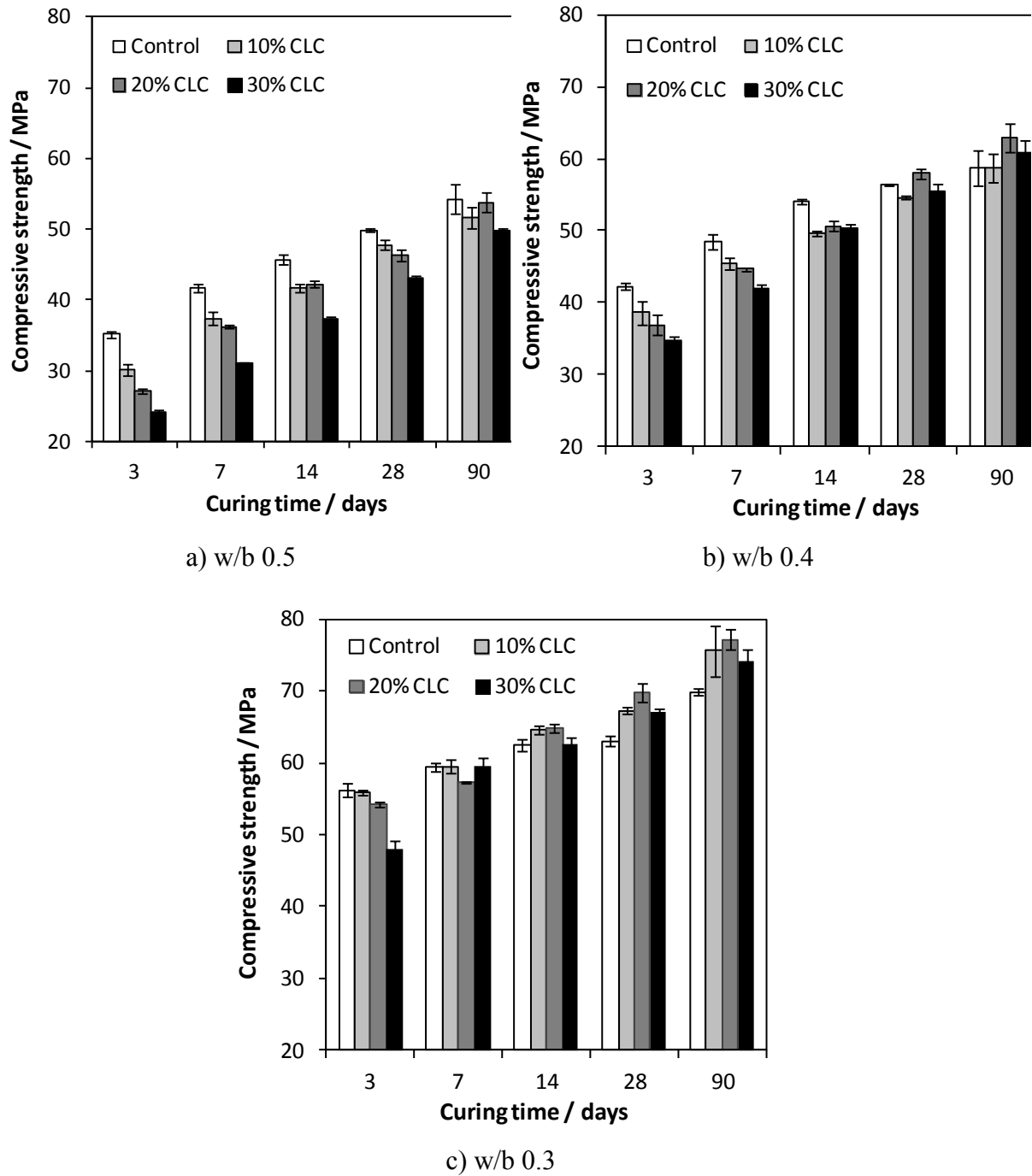
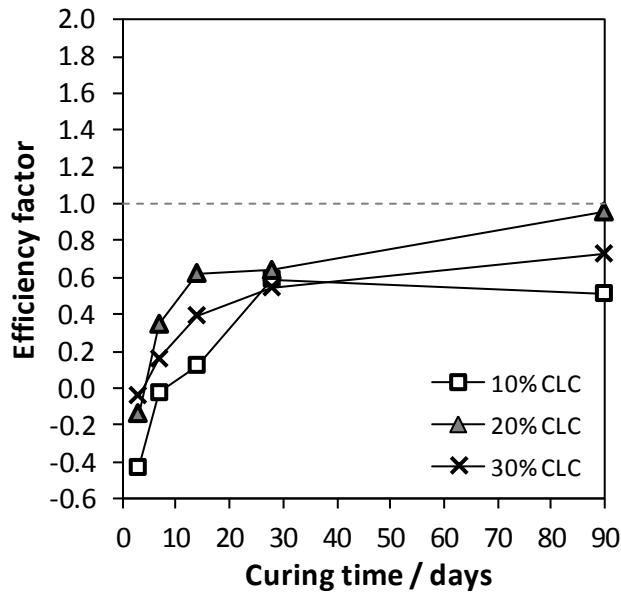
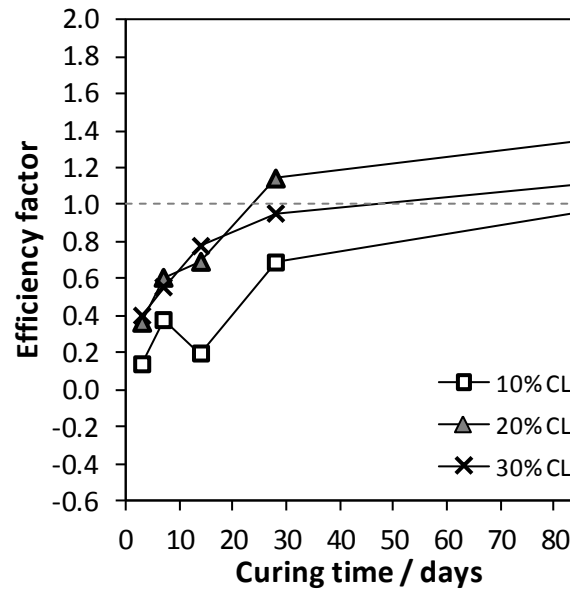


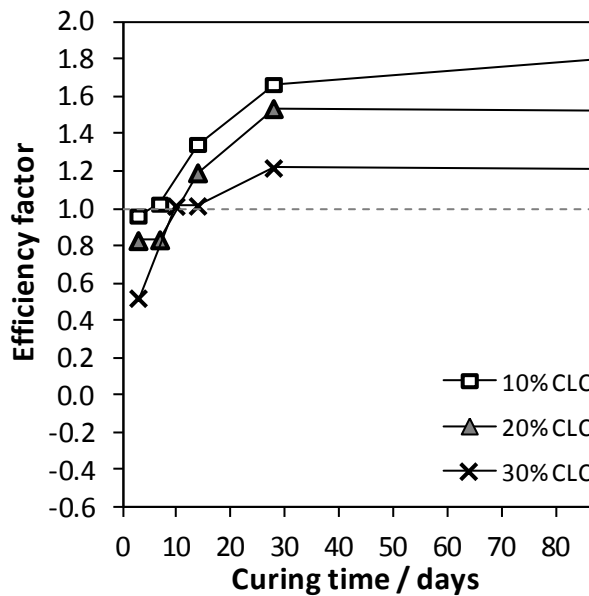
Fig. 10. Strength development of concrete samples made with 0, 10, 20 and 30 wt.% replacement of CEM I by London clay calcined at 900 °C. a) w/b = 0.5, b) w/b = 0.4 and c) w/b = 0.3.



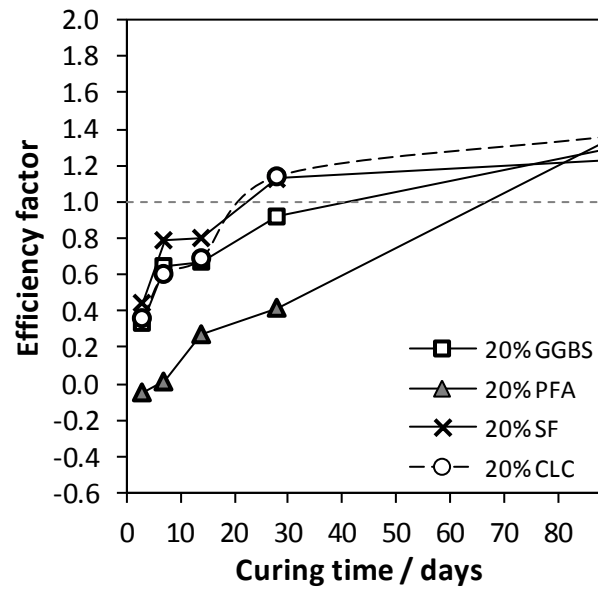
a) w/b 0.5



b) w/b 0.4



c) w/b 0.3



d) 20% replacement of various SCMs, w/b 0.4

Fig. 11. Strength efficiency factors of calcined London clay (900°C) in concretes made with various w/b ratios and replacement levels. a) w/b = 0.5, b) w/b = 0.4 and c) w/b = 0.3. d) efficiency factors for GGBS, PFA, SF and calcined London clay (900°C) at 20 wt. % replacement level and 0.4 w/b ratio.