DEVELOPING SUPPLEMENTARY CEMENTITIOUS MATERIALS FROM WASTE LONDON CLAY

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A thesis submitted to Imperial College London for the degree of Doctor of Philosophy

October 2016

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Declaration of Originality

I, DING ZHOU, confirm that the work presented in this PhD thesis is my own original work, and all else has been appropriately referenced.

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Abstract

Major tunnelling projects in London have generated enormous amounts of excavated clay, and there will be even larger production of excavated London clay in the next few years. This research focuses on investigating the technical feasibility of processing excavated London clay into a supplementary cementitious material (SCM) suitable for the use in concrete.

Excavated London clay was calcined at a range of temperatures between 600 and 1000 °C for 2 hours. The as-received and calcined London clay samples were characterized using techniques including XRF, XRD, FTIR, TGA/DTG, ICP, SEM, nitrogen adsorption, laser diffraction, isothermal conduction calorimetry and pycnometry. London clay is a complex mix of various types of clay and non-clay minerals, such as kaolinite (~30.2 wt.%), illite (~11.9 wt.%), montmorillonite (~41.3 wt.%), chlorite, pyrite, goethite, feldspar and quartz (~16.6 wt.%). Calcining excavated London clay resulted in oxidation, dehydration, dehydroxylation, amorphization and recrystallization, causing significant compositional and structural changes to clay and non-clay minerals. The degree of change depended on the calcining temperature. At 600 °C, kaolinite was entirely dehydroxylated, and the removal of octahedral hydroxyls led to a collapse of the 1:1 layered structure. As a result, metakaolin was formed. In contrast, the dehydroxylation of illite and montmorillonite started below 600 °C but finished at around 800 °C. Additionally, the two clay minerals did not suffer significant loss in crystallinity from complete dehydroxylation. The collapse of the 2:1 layered structure of illite and montmorillonite took place only when the calcining temperature was 900 °C and above. It was also observed that the recrystallization of spinel occurred above 950 °C.

The assessment of pozzolanic reactivity for calcined London clays was performed using the strength activity index (SAI) test, Frattini test, portlandite consumption test and the Chapelle test. The results showed that excavated London clay can be transformed into a SCM by calcining, and the optimum calcining temperature is 900 °C. The decrease at 950 °C can be attributed to the occurrence of spinel recrystallization.

London clay calcined at 900 °C was used to produce concrete at replacement levels up to 30 wt.% and three water-to-binder ratios (0.3, 0.4, 0.5). A CEM-I replacement of
up to 30 wt.% showed no detrimental effect on workability or the compressive strength of concrete. In addition, the concrete with 30 wt.% of CEM-I substituted by calcined London clay and a w/b ratio of 0.3 had greater strength than control concrete after 28 days curing. At a replacement of 20 wt.% and a w/b ratio of 0.4, the concrete containing calcined London clay had similar 90-day compressive strength to those incorporating pulverised fuel ash, ground granulated blastfurnace slag and silica fume.

Carbon emission estimation showed that a 30 wt.% substitution of CEM-I by calcined London clay in concrete produces ~27% less CO₂ emission compared to 100 wt.% CEM-I.

This study has demonstrated that it is technically feasible to use calcined London clay as a supplementary cementitious material for use in concrete.
Acknowledgement

First of all, I would like to sincerely thank my parents, Mr Yaping Zhou and Ms Qin Zu. They have always unconditionally supported every decision I made in my life since I was still very young, allowing me to grow up in a way I want. I had had a very happy childhood and an unforgettable schoolboy period, during which I was finely protected and well educated by them. All things that they have offered to me make me feel so much thankful that I am their son, which is also I am always proud of. They participated in all of my best time so far, and they will forever be the first two persons who I would like to share good news with.

Secondly, I would like to say a big ‘thank you’ to my supervisor, Professor Chris Cheeseman. He is absolutely the key person in both my MSc study and PhD study. Although I had a fairly slow start in the first year due to various reasons, he did not give up, and encouraged me to drive my research back to the correct track. Everything started to proceed smoothly from the second year onwards. I cannot accomplish that without his help.

I would also like to express my deep gratitude to Dr Geoff Fowler and Ms Carol Edwards. Both of them helped me so much inside and outside the lab, and they are always dedicated and patient. Thankfulness also goes to Dr Hong Wong, who examined my early stage and late stage assessments, and made massive contribution to my research. The other current or former staff of Department of Civil and Environmental Engineering that I would like to thank include Ms Fionnuala Ni Dhonnabhain, Ms Judith Barritt, Ms Nicole Lau, Ms Eugenia Kidd, Ms Angela Frederick, Mr Andrew Morris, Mr Stefan Algar. I would also like to acknowledge a number of useful discussions I had during the course of this research with Dr Mark Tyrer, Mr Philip Owens and Mr Richard Boarder. I must also appreciate that the Advanced & Innovative Materials lab at UCL kindly allowed me to use their isothermal conduction calorimeter. This was important for my research.

I would like to mention a few names of my friends/colleagues and thank them, who have made my outside-study life in the past four years pleasant and enjoyable. They are Mr Richard Wang, Dr Wenjie Cui, Dr Wenzheng Yu, Mr Nicolas Schaeffer, Mr Hooman Armand and other nice people from the EWRE and the whole department.
will never forget the hot summer of 2015 I spent with Richard. Every single drop of the sweat we left in the structures lab is paying off now. Wenjie is an ideal flatmate. I really enjoy his flavoured cooking, and I hope he enjoys my dish-washing as well. Wenzheng is always inspiring me to do better and achieve more in my research, and I have learnt a lot useful from him.

Next I would like to acknowledge the financial support from China Scholarship Council. The scholarship really made my life in London easier.

Lastly, I would like to quote part of a famous chant to finish this acknowledgement, because it represents a different side of my life in the UK.

Glory Glory Man United! As the reds go marching on on on!
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Chapter 1 INTRODUCTION
1.1 General introduction

Global Portland cement production reached 4.1 billion tonnes in 2015, increasing by 24% since 2010 (U.S. Geological Survey, 2016). It is expected that this figure is unlikely to fall in the next few years. This is because many developing countries are experiencing rapid urbanization and population growth, making the demand for housing and infrastructure development greater than ever before. Portland cement manufacture is highly carbon- and energy-intensive. The manufacture of 1 tonne of Portland cement generates 730~990 kg of CO$_2$ emission (Hasanbeigi et al, 2012). Given the huge amount of Portland cement produced globally, it is estimated that about 5% of anthropogenic CO$_2$ emissions per annum is produced from the cement manufacturing industry (Worrell et al, 2001).

The progresses on reducing the cement-manufacture-related CO$_2$ emissions and making cement greener have never stopped since the critical environmental impacts of global warming emerged. Clinker content substitution by less carbon-intensive materials is widely acknowledged as an effective way to reduce the overall CO$_2$ emission associated with the cement manufacturing. It can be achieved by having Portland cement partially replaced in concrete by supplementary cementitious materials (SCMs), which are mostly derived from other industries as unwanted by-products. Pulverized fuel ash (PFA) from coal-fired power plants, ground granulated blastfurnace slag (GGBS) from steel-making industry, and silica fume from silicon alloy industry are the most commonly used SCMs by worldwide manufacturers of cement and concrete. SCMs feature a shared property that they, in finely divided form, can react with Ca(OH)$_2$ in the presence of water to form a variety of excess cementitious phases. In a blended cement system containing SCM, where Ca(OH)$_2$ is provided by the hydration of Portland cement, the formed excess cementitious phase can generally fill capillary pores in the cement matrix, reducing porosity of the system. Consequently, this leads to enhanced long-term strength and improved durability for the system, as compared to a pure Portland cement system (Thomas, 2013). Additionally, there is another important benefit from using the SCMs derived from industrial by-products in concrete. The unwanted by-products or wastes from an industry (i.e. PFA, GGBS, silica fume) become resources for another industry (i.e. concrete), which converts
linear economies that were independent of each other previously, into an integrated circular economy.

However, the stability of the long-term supply of PFA, GGBS and silica fume has become questionable, and it is very likely that the availability of these SCMs would decrease (Mann, 2014). The global tendency towards less reliance on fossil fuels for energy generation can significantly reduce the supply of PFA in the long term. Similarly, the production of steel in Europe is expected to fall, with associated reduction in the availability of cementitious slag and silica fume (Worrell et al, 2001). In the UK, PFA has been in short supply in recent years due to coal power plants having increasingly opted for biomass and gases rather than coal as resources. The domestic supply of GGBS has also suffered significant shortages (Mann, 2014). The import of such SCMs from outside the UK has been overwhelmingly relied on. Alternative SCM is therefore expected to arise.

Calcined clay is regarded as an appropriate alternative to the existing SCMs that are experiencing serious supply issues. The application of calcined clay as a binder was originally found in Roman concrete. However, the material has not been extensively used by modern construction industries, partly due to inconsistency in mineralogical composition across different sources. In addition, it is not yet commercially available, which may also be responsible. The unique advantage of calcined clay lies in the wide availability of clay materials as well as the easy accessibility of most clay sources. The excellent availability of clays, together with the highly potential unavailability of existing SCMs and the increasingly stringent limitation of carbon emissions, may open a new era for the global cement industry.

The major tunnelling associated with Crossrail, a 118-kilometre-long railway project in London, had produced 7 million tonnes of excavated London clay. Most of the clay was reused in Southeast England for creating a wetland nature reserve, recreational facilities, agricultural and industrial lands (Crossrail, 2015a). For example, Wallasea Island in Essex, England is an artificial wetland nature reserve built using the clay. As these applications apparently did not get the most out of the value of excavated London clay, developing the clay into a SCM would appear to be a higher value reuse. More importantly, the direct recycling of excavation spoils into the very construction projects that generate them is feasible, which will make London-based infrastructure
projects part of the circular economy whilst significantly reducing building-embodied carbon. Furthermore, the constructions of Thames Tideway Tunnel, Crossrail II and HS2, which is a high speed railway linking London with several other major cities in the UK, are due to commence in the very near future, which will also be generating a huge quantity of excavated London clay. The abundant supply of excavated clay in London in next few years will give calcined clay a great opportunity to occupy the domestic SCM market.

London clay is essentially a complex mixture of various clay and non-clay minerals. Its mineralogy is significantly more sophisticated than kaolinitic clay, which is often used to produce metakaolin by calcining. Due to the variation in lattice structure, different types of clay minerals need different calcining temperatures to get transformed into amorphous phase, which can react with Ca(OH)_2 and water to form cementitious phases. For calcined London clay to be used as an alternative SCM in concrete, it is crucial to ensure there is enough amorphous phase transformed from clay minerals by means of calcining. Also it is reasonable to expect that there would be an optimum calcining temperature that can result in the maximum amount of amorphous phase for calcined London clay. The determination of the optimum calcining temperature for London clay is the key objective in this study. The aim and other objectives of this work are presented in the following chapter.
Chapter 2 AIM, OBJECTIVES AND EXPERIMENTAL APPROACH
2.1 Aim and objectives

The aim of this research was to investigate and optimize the processing required to transform excavated London clay into a SCM suitable for the use in concrete, and to evaluate the carbon emission savings of using calcined London clay as a SCM in concrete.

This has been achieved by meeting the following objectives:

1. Understanding as-received London clay in terms of chemical compositions, mineralogical compositions, thermogravimetric behaviour, and particle properties (fineness, porosity, morphology, etc.);
2. Understanding how different constituent clay minerals respond, structurally and chemically, to the intense heating of different levels;
3. Determining the optimum calcining temperature at which the highest pozzolanic reactivity can be achieved, and understanding the reasons why it appears to be the optimum temperature;
4. Investigating the effects of partially replacing Portland cement with calcined London clay on the workability of fresh concrete and on the compressive strength development of hardened concrete;
5. Estimating the amount of carbon emission that can be saved by using calcined London clay as a SCM in concrete.
2.2 Experimental approach

Experimental work was divided into six parts to fulfil all the objectives of this study. Because excavated London clay was supplied directly from a tunnelling site in the as-produced form, material processing was necessary including drying and grinding to break up the dried clay and produce a suitable powdered sample.

Calcining was the next step. The dry and powdered clay, which is consistently referred to as the as-received London clay throughout this thesis, was calcined at various temperatures (i.e. 600, 700, 800, 850, 900, 950 and 1000 °C) for a period of 2 hours, which was selected to ensure that as-received clay can be calcined completely at any temperature. It is worth mentioning that 850 and 950 °C were added later on to narrow down the temperature window and improve the accuracy in determining the optimum calcining temperature, after the range of 800–1000 °C was found to be more likely to accommodate that optimum temperature.

The as-received and calcined clay samples were characterized to understand the mineralogical, structural, physical and chemical properties. A number of techniques were employed to achieve characterization, including XRF for chemical composition, pycnometry for particle density, laser diffraction for particle fineness, SEM for particle morphology, XRD for mineralogical composition, FTIR for mineralogical composition, TGA/DTG for thermogravimetric behaviour, ICP for leaching property, nitrogen adsorption for particle surface area and porosity, and isothermal conduction calorimetry for blended cement hydration heat.

Clay calcined at different temperatures may exhibit different degrees of pozzolanic reactivity. All the calcined samples in this study were assessed with respect to pozzolanic reactivity, aiming at finding out the optimum calcining temperature at which London clay shows the highest pozzolanic reactivity. The adopted methods included Frattini test, portlandite consumption test and Chapelle test, which are considered direct methods, and SAI test, a typical indirect method.

London clay sample calcined at the optimum temperature was used to make concrete specimens at different cement replacement levels (i.e. 10%, 20%, 30%) and different water-to-binder ratios (i.e. 0.3, 0.4, 0.5). Concrete specimens containing PFA, GGBS and silica fume were also prepared. For all the mixes, the workability of fresh concrete
Chapter 2 Aim, objectives and experimental approach

and the compressive strengths up to 90 days of hardened concrete were tested and compared. Metakaolin is another well-known SCM but it was not considered for any experimental work of this study, due to the relatively poor prevalence in the concrete industry.

A reasonable estimation of the carbon emission savings by using calcined London clay as a SCM in concrete was also presented.

Figure 2.1 provides an overview of the structure of this study.

**Figure 2.1** An overview of the structure of this study
Chapter 3 RESEARCH BACKGROUND
3.1 Portland cement

3.1.1 Introduction to Portland cement

BS EN 197-1 (2011) defines cement as ‘a hydraulic binder, i.e. a finely ground inorganic material which, when mixed with water, forms a paste which sets and hardens by means of hydration reactions and processes and which, after hardening, retains its strength and stability even under water.’

The use of cement has had tremendous historical significance in the development of human civilisation, leading to the emergence of artefacts ranging from the over 2000 years old Roman Pantheon to modern skyscrapers and motorways (Amato, 2013). The method of manufacturing cement has very much evolved from simply mixing volcanic ashes with lime to intensively heating a sophisticated mixture of limestone, clay, shale and other supporting materials at a temperature of up to 1450 °C. The final product of the latter is known as Portland cement, which was originally patented by an Englishman, Joseph Aspdin in 1824, and by far the most common type of cement for general use across the world (Neville, 1996).

As a result of the rapid evolution of modern civilisation and modern industry during the recent one and half century, the global demand for cement has boomed exponentially. According to U.S. Geological Survey (2016), the world cement production hit 4.1 billion tonnes in 2015, 24 % greater than the figure in 2010. Moreover, the total world production of cement has been expected to reach 4.4 and 4.8 billion tonnes in 2020 and 2030, respectively, as shown in Figure 3.1 (VDZ, 2013). China, India, US, Brazil, Turkey and Russia are the largest countries in the world with respect to cement manufacturing. In the UK, the amount of cement produced in 2014 was reportedly around 9 million tonnes (Department for Business, Innovation and Skills, 2015).
3.1.2 The manufacture of Portland cement

Portland cement is primarily composed of tricalcium silicate (C\textsubscript{3}S), dicalcium silicate (C\textsubscript{2}S), tricalcium aluminate (C\textsubscript{3}A) and tetracalcium aluminoferrite (C\textsubscript{4}AF), the typical mass percentages of which are 45~75 \%, 7~32 \%, 0~13 \% and 0~18 \%, respectively. The manufacturing process of Portland cement is schematically illustrated in Figure 3.2, and described in the following paragraph.

In addition to limestone, which is the major raw material, clay, shale and sand are necessarily used as the other raw materials. A range of mechanical processing including mixing, crushing and grinding are carried out to produce a homogeneous blend of raw materials, which will be called the raw ‘meal’ below. A pre-heater is normally employed, heating part of the raw meal before that enters the rotary kiln, where the interior temperature can reach about 1450 °C. Due to the intensive heating, a sequence of physical and chemical reactions take place for the raw meal in the pre-heater and, particularly, the rotary kiln. This leads to the formation of a sintering product, which is known as ‘clinker’ and is essentially composed of C\textsubscript{3}S, C\textsubscript{2}S, C\textsubscript{3}A and C\textsubscript{4}AF. The clinker is allowed to cool on departure from the rotary kiln. A small amount of gypsum (typically ~5 wt.\%) is added at this point, helping achieve the desired setting quality in the final product. At last, the mixture of clinker and gypsum is finely ground
to form the Portland cement powder as the final product. Cement silos are used to store the product before this is out for packing or delivering.

According to BS EN 197-1, clinker, as the major content of Portland cement, is formed by sintering a precisely designed mixture of raw materials containing CaO, SiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$ and small quantities of other materials. Neville (1996) suggested the typical chemical compositions of Portland cement clinker, which is shown in Table 3.1.

**Table 3.1** Typical chemical compositions of Portland cement clinker (Neville, 1996)

<table>
<thead>
<tr>
<th>Oxides</th>
<th>Content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>60–67</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>17–25</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>3–8</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>0.5–6.0</td>
</tr>
<tr>
<td>MgO</td>
<td>0.5–4.0</td>
</tr>
<tr>
<td>Alkalis</td>
<td>0.3–1.2</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>2.0–3.5</td>
</tr>
</tbody>
</table>
3.1.3 The classification of common cements

In addition to gypsum, some materials, such as pulverised fuel ash (PFA or coal fly ash), ground granulated blastfurnace slag (GGBS) and silica fume, may be added as partial clinker substitute to produce blended cements. Depending on the type and amount of such material added, cement is classified into five categories in BS EN 197-1. Table 3.2 gives the detailed classification of common cements.

Table 3.2 Classification of common cements (BS EN 197-1:2011)

<table>
<thead>
<tr>
<th>Cement type</th>
<th>Designation</th>
<th>Composition (wt.%)</th>
<th>Minor constituents</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Clinker</td>
<td>Other main constituents</td>
</tr>
<tr>
<td>CEM I</td>
<td>Portland cement</td>
<td>95-100</td>
<td>N/A</td>
</tr>
<tr>
<td>CEM II /A</td>
<td>Portland silica fume cement</td>
<td>90-94</td>
<td>Silica fume</td>
</tr>
<tr>
<td></td>
<td>Portland slag cement</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Portland pozzolana cement</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Portland fly ash cement</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Portland burnt shale cement</td>
<td>80-94</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Portland limestone cement</td>
<td>65-79</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Portland composite cement</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CEM III /A</td>
<td>Blastfurnace cement</td>
<td>35-64</td>
<td></td>
</tr>
<tr>
<td></td>
<td>/ B</td>
<td>20-34</td>
<td>Blastfurnace slag</td>
</tr>
<tr>
<td></td>
<td>/ C</td>
<td>5-19</td>
<td></td>
</tr>
<tr>
<td>CEM IV /A</td>
<td>Pozzolanic cement</td>
<td>65-89</td>
<td></td>
</tr>
<tr>
<td></td>
<td>/ B</td>
<td>45-64</td>
<td>Pozzolana</td>
</tr>
<tr>
<td>CEM V /A</td>
<td>Composite cement</td>
<td>40-64</td>
<td>Blastfurnace slag</td>
</tr>
<tr>
<td></td>
<td>/ B</td>
<td>20-38</td>
<td>and pozzolana</td>
</tr>
</tbody>
</table>
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3.1.4 Cement hydration

Cement is a hydraulic material which reacts with water to form a range of compounds. In construction works, owing to this hydraulic character, it is used to bind aggregates, such as stones, gravels and sands, for producing concrete.

Studies and investigations have been carried out by scientists to understand the underlying mechanisms of cement hydration, and enormous progress has by far been achieved on the development of this knowledge. For example, it is now widely acknowledged that cement hydration is fundamentally a dissolution-precipitation process (Scrivener & Nonat, 2011). Bullard et al (2011) reviewed preceding important works and concluded that cement hydration involves a sequence of coupled chemical processes, which are dissolution/dissociation, diffusion, growth, nucleation, complexation and adsorption. In addition, the rate of each process is determined by both the nature of the process and the state of the system at that moment. However, there are still many controversies in understanding the kinetics of cement hydration and the mechanisms at the molecular scale.

Cement hydration reactions are highly exothermic, and therefore the evolution of the heat released from hydration can be used to characterize the rate of hydration. Portland cement (CEM-I) is typically composed of $C_3S$ (alite), $C_2S$ (belite), $C_3A$, $C_4AF$ and gypsum. The hydration of $C_3S$ takes place immediately on wetting, producing calcium silicate hydrates (C-S-H) gel and calcium hydroxide (portlandite). This leads to the build-up of early strength. Figure 3.3 shows how the rate of $C_3S$ hydration is typically changed within the first 24 hours on wetting (Bullard et al, 2011). The hydration of $C_3S$ can, to a large extent, reflect the behaviour of cement (Neville, 1996). In contrast, $C_2S$ hydrates at a significantly lower rate but the hydration products are ultimately the same as those of $C_3S$. It is reported that on complete hydration, $C_3S$ can produce more than twice as much portlandite as $C_2S$ does, in spite of the approximately same water consumption (Neville, 1996). The hydration reaction of pure $C_3A$ phase is very rapid, with $C_3A$H$_6$ formed as the final product. Such an instantaneous reaction can cause immediate setting to cement paste, which is not favoured in cement applications because the workability is significantly impaired. In order to prevent the instant setting, calcium sulphate is necessarily added into cement, and gypsum ($CaSO_4 \cdot 2H_2O$) is most commonly used. The reaction between $C_3A$,
gypsum and water initially results in the formation of ettringite (AFt, chemical formula: $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$). However, when the added gypsum is completely depleted later on but C$_3$A is still remaining, AFt can be converted into AFm phase (chemical formula: $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O}$), which contains less sulphate content than the former. Figure 3.4 explains how the heat evolution of C$_3$A hydration can be affected by the increasing amount of gypsum addition (Minard et al, 2007). It is obvious that the length of the duration in between the formation of AFt (first peak) and the conversion of AFt to AFm (second peak) is positively related to the amount of gypsum added. At relatively late ages, when AFm phase is saturated, C$_3$AH$_6$ can be formed by the direct hydration of C$_3$A. C$_4$AF behaves similarly to C$_3$A in the presence of water, with the primary product of hydration being C$_3$AH$_6$ as well. In addition, the hydration can also be retarded by reacting with gypsum to form calcium sulfoferrite and calcium sulfoaluminate. More about the heat evolution of cement hydration will be discussed in details in Section 5.10.

As a summary, the formation and hydration of Portland cement is briefly illustrated in Figure 3.5.

![Figure 3.3 Rate of alite hydration as a function of time given by isothermal calorimetry measurements (Bullard et al, 2011)](image-url)
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Figure 3.4 Heat evolution rate curves during the hydration of C\textsubscript{3}A in solutions saturated with respect to portlandite (liquid-to-solid mass ratio = 25) carried out with increasing quantities of gypsum (Minard et al, 2007)

<table>
<thead>
<tr>
<th>Component elements</th>
<th>Si</th>
<th>Ca</th>
<th>Al</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Component oxides</td>
<td>SiO\textsubscript{2}</td>
<td>CaO</td>
<td>Al\textsubscript{2}O\textsubscript{3}</td>
<td>FeO\textsubscript{3}</td>
</tr>
<tr>
<td>Cement compounds</td>
<td>C\textsubscript{3}S</td>
<td>C\textsubscript{2}S</td>
<td>C\textsubscript{3}A</td>
<td>C\textsubscript{4}AF</td>
</tr>
<tr>
<td>Portland cement</td>
<td>C: CaO;</td>
<td>S: SiO\textsubscript{2};</td>
<td>A: Al\textsubscript{2}O\textsubscript{3};</td>
<td>F: Fe\textsubscript{2}O\textsubscript{3};</td>
</tr>
<tr>
<td>Water</td>
<td>H: H\textsubscript{2}O;</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Main hydration products</td>
<td>A\textsubscript{Ft}: Al\textsubscript{2}O\textsubscript{3}-Fe\textsubscript{2}O\textsubscript{3-tri};</td>
<td>AFm: Al\textsubscript{2}O\textsubscript{3}-Fe\textsubscript{2}O\textsubscript{3-mono};</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 3.5 Brief illustration of the formation and hydration of Portland cement, modified from the work of Neville (1996)
3.1.5 CO₂ emissions associated with cement production

The cement industry is highly energy-intensive and carbon-intensive, and it is considered the second largest CO₂-emitting industry, only after power plants (Ishak & Hashim, 2015). It was reported that manufacturing 1 tonne of cement generates 730-990 kg of CO₂ emission (Hasanbeigi et al, 2012). According to an up-to-date report published by PBL Netherlands Environmental Assessment Agency (Olivier et al, 2015), cement production accounts for roughly 8% of global CO₂ emissions in 2014, which is about 2.9 billion tonnes. In the UK, the CO₂ emissions from the manufacture of cement was reportedly about 6.6 million tonnes in 2014 (Office for National Statistics, 2016).

In the manufacture of cement, CO₂ emissions originate from two main sources. Limestone, as the dominant constituent of the raw meal, is decomposed by calcining into calcium oxide (CaO) and CO₂. This occurs both in the pre-heater and in the rotary kiln, which is shown in Figure 3.2. To produce the extreme heat required to support calcining the raw meal, fossil fuels are burnt, such as oil, coal and natural gas. The combustion of these fossil fuels can result in a huge amount of CO₂, which is the second of the two sources referred to. According to Cement Technology Roadmap 2009 (IEA & WBCSD, 2009), the CO₂ generated from the decomposition of limestone accounts for 60-65% of total emission while the remaining share is contributed by the combustion of fossil fuels. In addition, the electricity consumed by plant machinery and the transportation of final product can also contribute CO₂ emissions but those are minor as compared to the two main sources.

Given the tremendous cement production every year, the need of reducing the cement-manufacture-related CO₂ emissions and making cement greener is urgent. For the cement industry, a possible transition path to achieve the target of halving the current CO₂ emissions by 2050 is outlined in Cement Technology Roadmap 2009 (IEA & WBCSD, 2009). Four key carbon emissions reduction approaches were proposed and highlighted, as shown in Figure 3.6.
The improvement of energy efficiency and the use of alternative fuels had reportedly achieved great developments in recent years (Schneider et al, 2011). Carbon capture and storage (CCS) is an effective technology to prevent CO$_2$ from being released into the atmosphere but a widespread implementation of it in cement plants has still been impractical due to economic, technical and legal barriers (Benhelal et al, 2013). Using cementitious industrial by-products for clinker substitution can considerably reduce relevant CO$_2$ emissions. It was reported that the average clinker fractions in world cement production had decreased to between 60 and 80% by 2014 (Olivier et al, 2015). The aim of this study essentially conforms to the approach of clinker substitution.

**Figure 3.6** Carbon emissions reduction approaches (IEA & WBCSD, 2009)
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3.2 Concrete

3.2.1 Brief introduction to concrete

Concrete is an artificial composite material, manufactured by mixing cement with water and a combination of fine and coarse aggregates. In construction works, the adopted mix proportions can vary considerably, depending on a number of factors, such as the types of concrete applications, the properties of aggregates and the employment of additives (i.e. super-plasticizers). Owing to the massive production of cement around the world, concrete was reportedly the most manufactured and consumed artificial products on the earth, and the second most consumed substance only after water. In addition, if the population of the whole world is taken as a reference for comparison, 3 tonnes of concrete are consumed per capita each year (Rubenstein, 2012).

Concrete can be classified in terms of density as well as compressive strength, which is shown in Table 3.3 and 3.4 (Li, 2011).

**Table 3.3 Classification of concrete by density (Li, 2011)**

<table>
<thead>
<tr>
<th>Classification</th>
<th>Density (kg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultra-light weight</td>
<td>&lt;1200</td>
</tr>
<tr>
<td>Lightweight</td>
<td>1400~1800</td>
</tr>
<tr>
<td>Normal-weight</td>
<td>~2400</td>
</tr>
<tr>
<td>Heavyweight</td>
<td>&gt;3200</td>
</tr>
</tbody>
</table>

**Table 3.4 Classification of concrete by compressive strength (Li, 2011)**

<table>
<thead>
<tr>
<th>Classification</th>
<th>Compressive strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low-strength</td>
<td>&lt;20</td>
</tr>
<tr>
<td>Moderate-Strength</td>
<td>20~50</td>
</tr>
<tr>
<td>High-strength</td>
<td>50~150</td>
</tr>
<tr>
<td>Ultra-high-strength</td>
<td>&gt;150</td>
</tr>
</tbody>
</table>

3.2.2 Aggregates

As aggregates occupy the majority of the volume of concrete, the properties of aggregates can significantly affect the performances of concrete with respect to
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strength and durability. Despite the reason of largely using aggregates in concrete being derived from economic considerations, it has currently been realised that the employment of aggregates can lead to a higher volume stability and better durability than using hydrated cement paste alone (Neville, 1996). In the manufacture of good quality concrete, two size groups of aggregates (fine and coarse) are always used. The most common fine aggregate is sand with a particle diameter of less than 5 mm, while coarse aggregate is usually greater than 5 mm in particle fineness (Neville, 1996). In BS EN 12620:2013, the aggregate with a particle diameter less than or equal to 4 mm is defined as fine aggregate, and coarse aggregate is larger than 4 mm in particle diameter.

The water absorption and moisture content of aggregates, which vary on a case-by-case basis, are directly related with the actual amount of water used for cement hydration because the aggregates in a water-unsaturated state can absorb some of the added water whilst the wet can bring extra water into concrete. It is necessary to, before mixing starts, work out the water absorption and moisture content of employed aggregates and subsequently apply adjustment to the amount of water weighed in accordance with the designed mix proportions, ensuring the hydration of cement can work at the designed w/b ratio. Figure 3.7 presents the different water-absorbing statuses of aggregates (Neville, 1996).

![Figure 3.7 Water-absorbing statuses of aggregates (Neville, 1996)](image)

**Figure 3.7** Water-absorbing statuses of aggregates (Neville, 1996)

### 3.2.3 Workability of concrete

For any particular type of concrete, a good workability normally concerns maximum possible density, elimination of entrapped air, homogeneity and full compaction. In most cases, all these can be achieved by means of vibration. There are a number of
factors that can affect the workability of concrete. Among them, it is easy to understand that water content is the main factor because the amount of water directly determines the lubrication for the whole mixture. The maximum size, grading, shape and texture of aggregates are also critical to the workability of concrete (Neville, 1996). Slump test is the most extensively used method to measure the workability of concrete, which will be technically detailed in Section 4.2.6. According to BS 8500-1 (2015), for the samples tested in accordance with BS EN 12350-1 (2009), the slump test results can be divided into several classes, which are shown in Table 3.5.

### Table 3.5 Slump classes according to BS 8500-1

<table>
<thead>
<tr>
<th>Slump class</th>
<th>Slump Not less than (mm)</th>
<th>Slump Not more than (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>0</td>
<td>50</td>
</tr>
<tr>
<td>S2</td>
<td>40</td>
<td>100</td>
</tr>
<tr>
<td>S3</td>
<td>90</td>
<td>160</td>
</tr>
<tr>
<td>S4</td>
<td>150</td>
<td>220</td>
</tr>
<tr>
<td>S5</td>
<td>210</td>
<td>-</td>
</tr>
</tbody>
</table>

#### 3.2.4 Strength of concrete

Strength is extensively conceived as the most important and valuable characteristic of concrete, and it is primarily dependent on the cohesion of cement paste, the adhesion of cement paste to aggregate particles and the strength of aggregate itself (Neville, 1996). For a given type of aggregate, particularly natural aggregate, its own strength cannot be easily changed as it is the intrinsic property of aggregate. In contrast, the former two factors are more flexible because they are directly determined by the w/b ratio as well as the degree of compaction. Moreover, they can be, to some extent, time-dependent.

Strength of concrete is a general term, which practically includes three forms: compressive strength, tensile strength and flexural strength. Nevertheless, only the compressive strength of concrete is concerned in this thesis. For a fully-compacted concrete at a given curing age, the strength is inversely proportional to the w/b ratio, as shown in Figure 3.8 (Neville, 1996). If a high w/b ratio is adopted, water would be in excess of the amount required to completely hydrate cement. This can lead to an
increase in the porosity of concrete at late ages when the excess water is dried out. The strength of concrete is therefore adversely affected due to the increased porosity. At a low w/b ratio, it would be more difficult to achieve a full compaction of concrete, because of the relatively inferior workability, and hence vibration is very often required in that case.

**Figure 3.8** The relation between compressive strength and w/b ratio of concrete (Neville, 1996)

As cement hydration continues with curing time, the cohesion of cement paste and the adhesion of cement paste to aggregate particles are improved, and concrete gains strength, accordingly.
3.3 Supplementary cementitious materials (SCMs)

3.3.1 Introduction to SCMs

Clinker substitution by certain materials is an effective way to reduce CO\textsubscript{2} emissions associated with the manufacture of concrete. The term, supplementary cementitious materials (SCMs), defines a wide range of such materials that have been used to substitute clinker in concrete. They can be divided into two groups in terms of their origins, which are naturally-occurring materials and manufactured industrial by-products. Volcanic ash is a typical naturally-occurring SCM, and manufactured by-product SCMs include, for example, pulverized fuel ash (PFA), ground granulated blastfurnace slag (GGBS) and silica fume. The cement industry appeared to be more enthusiastic about employing the SCMs derived from industrial by-products in producing blended cement, where clinker content is partially replaced (Gartner, 2004). Despite the considerable variation in properties, different types of SCMs share the ability to participate in chemical reactions and form favoured compounds that supplement cement hydration products. Here then comes an alternative way of classification for SCMs. With regard to the types of the chemical reactions, SCMs can be divided into two groups: pozzolanic materials (pozzolan) and hydraulic materials. The majority of currently available SCMs are pozzolanic, such as volcanic ash, PFA, silica fume and metakaolin, whilst GGBS is considered latent hydraulic rather than pozzolanic.

The appropriate use of SCMs is favourable to the properties of concrete, such as long-term strength and durability in aggressive environment (Thomas, 2013). In addition, there is another important benefit from using the SCMs derived from industrial by-products in concrete. That is the conversion of several linear economy systems to an integrated circular economy. Specifically, the by-products or wastes of some industries (i.e. PFA from the electric power industry, GGBS from the steel industry) are reused, as resources by cement manufacturers to produce blended cements. By this way, the linear economy systems (i.e. electric power industry and steel industry), which used to sustain themselves independently, are somewhat integrated. This is illustrated in Figure 3.9.
The clinker substitution by SCMs has been widely implemented around the world. The global average cement clinker content in 2006 was reportedly 78%, and in China and Latin America it was lower than 75% (Barcelo et al, 2014). Olivier et al (2015) reported that the world average clinker fraction in 2014 was between 60 and 80%.

In the UK, PFA has, however, been in short supply in recent years because coal power plants have increasingly opted for biomass and gas rather than coal as resources. The domestic supply of GGBS has also suffered significant shortages (Mann, 2014). As a result, the import of these SCMs from outside the UK has been overwhelmingly relied on by the British cement and concrete industry. A more economical and sustainable solution to the supply issue of SCMs is therefore called for within the UK.

### 3.3.2 Pozzolanic reaction

Pozzolan (pozzolanic SCMs) is defined in ASTM C125-15b as ‘a siliceous or siliceous and aluminous material that in itself possesses little or no cementitious value but will, in finely divided form and in the presence of water, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties.’ Accordingly, pozzolanic reaction can be briefly explained as a chemical process that occurs between pozzolan and calcium hydroxide with the presence of water, and, as a result, leads to the formation of cementitious compounds. In any blended cement system where a pozzolan is used to partially replace clinker content, the calcium hydroxide generated from the hydration of alite and belite reacts with the
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Pozzolan. Normally, the amorphous content of a pozzolan is much more vulnerable to the attack of calcium hydroxide than the crystalline content.

With respect to chemical compositions, pozzolans are usually abundant in silica, alumina or both. The reaction between calcium hydroxide and silica content of a pozzolan can be expressed as follows (Helmuth, 1987).

\[ xCH + yS + zH \rightarrow C_xS_yH_z \]

The product \( C_xS_yH_z \) is calcium silicate hydrate, which is also referred to as C-S-H gel like the main hydration product of alite and belite. However, in terms of the C/S ratio, this C-S-H gel is lower than the latter, and the difference can vary depending on the age, type and replacement level of pozzolan (Thomas, 2013). The alumina content of pozzolans also reacts with calcium hydroxide, which can produce various phases including strätlingite or gehlenite hydrate (\( C_2ASH_8 \)), hydrogarnet (\( C_3ASH_6 \)) and calcium aluminate hydrate (\( C_4AH_{13} \)) (Thomas, 2013). For example, metakaolin (\( AS_2 \)) can react with calcium hydroxide to form, mainly, C-S-H, \( C_2ASH_8 \) and maybe some amounts of \( C_4AH_{13} \) (Helmuth, 1987; Massazza, 1998), which can be represented as follows.

\[ AS_2 + 3CH + zH \rightarrow CSH_{2.5} + C_2ASH_8 \]

The total quantity of calcium hydroxide that a given pozzolan can combine with is determined by the following factors: the nature of the reactive phases in the pozzolan, the \( SiO_2 \) content of these phases, the CH-to-pozzolan ratio and the curing time. In addition, the rate of pozzolanic reaction is dependent on the specific surface area of pozzolan, w/b ratio and temperature (Massazza, 1998).

3.3.3 Filler effect

When particles finer than cement are added into a mix and involved in cement hydration, they are capable of filling up the capillary pores between cement particles and act as nucleation sites, providing more space for the growth of cement hydration products. By this way, the hydration of cement is accelerated consequently. This is called filler effect (Oey et al, 2013). However, in practice, the term ‘filler’ usually refers to the material that is chemically inert in either of hydration reaction and pozzolanic reaction, such as quartz. Despite that, filler effect also applies to SCMs, and it even
starts working prior to pozzolanic reaction, which requires the release of calcium hydroxide from cement hydration.

### 3.3.4 SCMs

#### 3.3.4 a) Pulverized fuel ash (PFA)

PFA is coal fly ash or fly ash, and it is the substance collected electrostatically or mechanically by precipitators from the flue gases of coal power plants. A typical layout of coal power plant is given in Figure 3.10, where fly ash is among those highlighted (Flyash Australia, 2010). According to ASTM C618, fly ash can be divided into two classes, F and C, depending on the type of coal that generates it. Class F normally refers to the fly ash produced from burning anthracite or bituminous coal, and it is mainly siliceous. Class C fly ash is generated from the combustion of sub-bituminous or lignite coal, and it (>20% CaO) usually contains higher calcium content, as compared to Class F fly ash (<8% CaO). Both classes are very much pozzolanic, and it is known that Class C fly ash also has some hydraulic properties of its own (Neville, 1996).

![Figure 3.10 The flow of the ashes in a coal power plant (Flyash Australia, 2010)](image)

The utilization of PFA as a SCM in cement and concrete has been extensively studied and implemented. It was discovered under scanning electron microscopy that PFA
particles are predominantly in a spherical shape, as shown in Figure 3.11. The incorporation of PFA in concrete can considerably improve the workability at a given w/b ratio. Alternatively, for a given workability, it can reduce the water demand of concrete. This is because the spherical particles can act as ball-bearings to support water lubrication in the fresh concrete mix (Jones & McCarthy, 2005).

The properties of concrete containing PFA have been investigated and reported in many literatures for decades, such as Fraay, Bijen & de Haan (1989), Gopalan & Haque (1989, 1990), Bensted (1990), Butler (1990), Babu & Rao (1996), Siddique (2003), Rajamane, Peter & Ambily (2007), Rivera et al (2015), Han, Wang & Feng (2015) and Rafieizonooz et al (2016).

In addition, it is particularly worth mentioning again that cement and concrete industry in the UK is currently suffering from a domestic supply issue of PFA. This is because less coal has been burned to generate electricity in the UK, and, instead, biomass and gas have become the major resource for coal-fired power plants (Mann, 2014).

![Figure 3.11 Morphology of PFA particles](image)

3.3.4 b) Ground granulated blastfurnace slag (GGBS)

Ground granulated blastfurnace slag (GGBS) is a glassy material, as a by-product, obtained from the manufacture of pig iron in a blast furnace. It is estimated that
producing 1 tonne of pig iron can result in roughly 300 kg of GGBS (Neville, 1996). A typical layout of pig iron production is given in Figure 3.12 (IIMA, 2015), where GGBS is highlighted with a red box. In addition, it should be noted that quenching is particularly important in ensuring the slag is suitable for the use as a SCM, as it can prevent the recrystallization of some phases that may happen in the slag during slow cooling.

Despite the variation in chemical compositions and physical structure, depending on the employed pig iron manufacture process and on the cooling method of the slag, GGBS is predominantly composed of lime, silica and alumina, which is similar to Portland cement (Neville, 1996). However, typically, GGBS contains less calcium and more silica, as compared to Portland cement. Figure 3.13 shows a ternary SiO$_2$-CaO-Al$_2$O$_3$ phases diagram, which involves not only slag but also PFA, silica fume, natural pozzolan and Portland cement (Lothenbach, Scrivener & Hooton, 2011). In addition, Figure 3.14 shows the morphology of GGBS particles, which are angular.

**Figure 3.12** Pig iron production layout (IIMA, 2015)
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Figure 3.13 A ternary phase diagram of lime, silica and alumina (Lothenbach, Scrivener & Hooton, 2011)

Figure 3.14 Morphology of angular-shaped GGBS particles

It can be seen in Figure 3.13 that slag is closer than any other SCM to the area of Portland cement on the ternary phase diagram. On the other hand, GGBS resembles...
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Portland cement in hydraulic properties, which is a character unseen from other SCMs. To be precise, GGBS is widely considered latent hydraulic. As soon as it contacts water, a Si-rich impermeable layer, as the initial hydration product, forms on the surface of GGBS grains, which prevents the further hydration of unreacted GGBS grains (Thomas, 2013). Alkalis can act as an activator to break down the impermeable layer, allowing the hydration of GGBS to advance to form C-S-H. When GGBS is mixed with Portland cement, the calcium hydroxide produced by the hydration of Portland cement, alongside Na\(^+\) and K\(^+\) present in the pore solution, can work effectively as the alkali activator. Additionally, the hydration of GGBS-blended cement can generate less calcium hydroxide and more C-S-H, as compared to that of pure Portland cement, leading to a denser microstructure in the hydrated cement paste (Neville, 1996).

The hydraulic reactivity of GGBS is largely dependent on chemical composition. It is prescribed in BS EN 15167-1 that, for the use of GGBS in concrete and mortar, the chemical compositions of GGBS shall contain at least two-thirds by mass of the sum of CaO, MgO and SiO\(_2\), and the remainder shall contain Al\(_2\)O\(_3\). Moreover, the ratio by mass of CaO plus MgO to SiO\(_2\) shall not be less than 1.0.

In practice, there are several different ways to use GGBS as a construction material. Firstly, it can join limestone as a raw material and as an alternative source of calcium in the conventional manufacture of Portland cement to make clinker. Secondly, owing to the latent hydraulic properties, GGBS can be used on its own with the presence of an alkali activator. Moreover, it is often added to pure Portland cement clinker, followed by an inter-grinding of the two materials to produce blended cement. Alternatively, cement manufacturers can blend Portland cement powder with GGBS to make blended cement and bag that. Lastly, GGBS can be stored, bagged and fed into a mixer independently of Portland cement powder. By this way, concrete containing GGBS-blended cement is manufactured in situ (Neville, 1996).

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Currently in the UK, the domestic supply of GGBS is rather unsteady for the cement and concrete industry, due to the declining productivity of the UK steel industry (Mann, 2014). Consequently, the availability of GGBS largely depends on imports from outside the UK.

3.3.4 c) Silica fume

Silica fume is an ultrafine amorphous silica powder, produced as a by-product in the manufacture of silicon metals and ferrosilicon alloys from high purity quartz and coal. A schematic illustration of silica fume production process is given in Figure 3.15 (BMI, 2012). Silica fume is primarily composed of SiO₂ but the amount of SiO₂ content can vary depending on the type of alloy being produced. For a given silica fume, it is considered suitable for the use in concrete, provided that its SiO₂ content should not be less than 85% (Thomas, 2013). Morphologically, silica fume particles are spherical, and the average particle size is typically within the range of 100 to 200 nm. In addition, it has a low bulk density, which is typically around 200~300 kg/m³. Due to the high particle fineness and low bulk density, such silica fume is difficult and expensive to handle. To solve this, silica fume is often processed to a densified or slurried form prior to the use in concrete (Neville, 1996). Figure 3.16 shows densified silica fume particles.

![Silica fume production process](image)

**Figure 3.15** A typical layout of silicon metal and alloys production (BMI, 2012)
Silica fume is highly pozzolanic. However, when used in concrete to partially replace Portland cement content, it can substantially decrease the workability of the concrete, as compared to a concrete mix with 100% Portland cement content. In the contemporary concrete practice, silica fume is most commonly used in the dry densified form (Diamond & Sahu, 2006). The breakdown of silica fume agglomerates under conventional concrete mixing is largely attributed to the shear action of aggregates, but it is often incomplete (Baweja, Cao & Bucea, 2003; Diamond, Sahu & Thaulow, 2004). The remaining agglomerates of silica fume can trap part of the mixing water, which would otherwise contribute to the fluidity of the mixture (Kong et al., 2013; Juenger & Siddique, 2015). That consequently gives rise to water demand for concrete incorporating silica fume to maintain a good workability. Apart from adding more water, employing super-plasticisers can be an alternative method.

The various properties of concrete incorporating silica fume have been well studied and reported, such as Mehta & Gjorv (1982), Popovics (1993), Bentz & Stutzman (1994), Zhou, Barr & Lydon (1995), Babu & Prakash (1995), Bhanja & Sengupta (2005), Gonzalez-Fonteboa & Martinez-Abella (2008), Bagheri et al (2013), Zhang, Zhang & Yan (2016a) and Zhang, Zhang & Yan (2016b).
3.3.4 d) Metakaolin

Metakaolin is the dehydroxylated and amorphous form of kaolinite. In the industry, it refers to thermally activated high-purity kaolinitic clay. Kaolinitic clay can typically contain over 70% of kaolinite as the major ingredient, making it dominated by kaolinite in respect of properties. This is significantly different from many cases, where clays usually have much more complicated mineralogical compositions, such as the London clay investigated in this study. Details about kaolinite and other clay minerals will be introduced and discussed in the following sections and chapters.

Metakaolin was used in various construction applications as a SCM to partially replace Portland cement (Sabir, Wild & Bai, 2001). The first documented use of metakaolin in concrete as a SCM was for the construction of the Jupia Dam in Brazil in 1962, where approximately 250,000 metric tonnes of metakaolin was consumed (Saad, De Andrade & Paulon, 1982). However, metakaolin was still not commercially available until the mid-1990s (Rashad, 2013). The major limitation of using metakaolin in a long term period may be that high-purity kaolinitic clay is not readily available around the world.
3.4 Clay

3.4.1 Definitions of clay and clay mineral

Unlike Portland cement, PFA, GGBS and silica fume, there is still no such definition for clay and clay minerals uniformly accepted by different disciplines, users and producers. One of the well-known definitions was made by the joint nomenclature committees (JNCs) of the Association Internationale pour l'Etude des Argiles (AIPEA) and the Clay Minerals Society (CMS). Clay was defined as ‘a naturally occurring material composed primarily of fine-grained minerals, which is generally plastic at appropriate water contents and will harden when dried and fired.’ However, in practice, the accepted upper limit of particle size of the ‘fine-grained minerals’ varies among different disciplines and professions, mainly ranging from 1 µm to 4 µm (Bergaya & Lagaly, 2006). The JNCs also stated that the ‘plasticity’ refers to the property that a material can be moulded into a shape without rupturing when stress is applied, and that shape can be maintained after the dismissal of the stress.

The term ‘clay mineral’ is defined by the JNCs as ‘phyllosilicate minerals and minerals which impart plasticity to clay and which harden upon drying or firing.’ It should be noted from this definition that the JNCs proposed non-phyllosilicate minerals could qualify as clay minerals, provided that they can impart plasticity to clay, and harden upon firing or drying (Bergaya & Lagaly, 2006).

3.4.2 Geology and genesis of clay and clay minerals

Clay can form under different geological environments: weathering, sedimentation (or deposition), burial diagenesis and hydrothermal alteration, which vary considerably in temperature and pressure. Temperature is particularly important for clay formation, as it determines the rate at which clay is formed as well as the types and properties of clay minerals. In the four geological environments it can range from 4 °C (ocean bottom) to approximately 400 °C (hydrothermal alterations). Time is another critical factor affecting the mineralogical compositions and properties of clay formed. It usually can range from years to millions of years (i.e. burial diagenesis). If the environment temperature is relatively low, it would take a longer period of time to attain a certain type of clay mineralogy, and vice versa. Clay minerals are mostly formed as a result
of the interaction of rock-forming silicate minerals with water at or near the very surface of the earth, and this is particularly the case in weathering (Velde, 1995; Galán, 2006).

Weathering normally occurs below a temperature of 30 °C, and involves dissolution of rock and transformation of original rock-forming materials into clay minerals. Rock type, climatic condition (i.e. rainfall and temperature), time (i.e. the age of weathering profile), topography, and the content of organisms and organic matter are all critical to the weathering process. It should be noted that topography can influence the water/rock ratio through drainage. This ratio plays a key role in determining the type of chemical reactions and ultimately the type of clay minerals formed in weathering process. When water is present in a large amount, rock-forming materials appear to be unstable and some tend to be dissolved. The greater the renewal of water input (i.e. rainfall) is, the greater the dissolution of rock can be. When the ratio is equal to one, the dissolution can be mainly in an incongruent state, where certain elements enter the solution while the others remains in a solid state in the skeleton of the weathered rock. Among those remainders are formed clay minerals, having been hydrated and featuring characteristic crystalline structures significantly different from those of the original rock-forming minerals. The chemistry of the clay-forming interaction between rock and water is essentially the exchange of protons (H\(^+\)) for mobile monovalent and divalent cations in the minerals. Practically, a diversity of clay minerals can be formed under weathering. For example, kaolinite can be neoformed or transformed from muscovite and feldspar, and illite can be developed from micaceous minerals as well as muscovite. Vermiculite can derive from muscovite/biotite and chlorite through interstratified structures. Dioctahedral smectite can form either by alteration of basic silicates or from other clay minerals, such as illite and vermiculite (Velde, 1995; Galán, 2006).

The distribution of clay minerals formed under weathering is of interest to geologists. Vertically, in a soil profile developed under heavy rainfall, kaolinite usually appears on the upper layer of the soil, while montmorillonite and other clay minerals structurally complicated than kaolinite is always found beneath. From the perspective of horizontal distribution, climatic condition is the predominant factor. It has been discovered that, generally, illite and chlorite are more abundant than others in cold areas, while vermiculite and mixed-layer clay minerals are favoured in mild climates. Moreover, the areas where tropical or Mediterranean climates prevail are more favourable to the
growth of smectite. In wet tropical or equatorial climates, kaolinite is more favoured than other species (Velde, 1995; Galán, 2006).

Sedimentation follows weathering in the clay cycle. Aquatic environments, such as rivers, lakes, seas and oceans, can contain abundant sediments and sedimentary rocks, which are originally derived from the weathered crusts (mainly clays and rock-forming non-clay minerals) by the sequential activities of erosion, transportation and deposition. The erosion of clay-rich soils allows the mobility of clays, and it can be affected by several factors, including soil profile structure, humidity, clay mineralogy and climatic conditions. The transportation of clays is primarily carried out by streams and rivers with the ultimate destination being large bodies of water, such as seas and oceans. The deposition of migrated clays can spread from the mouth of rivers to the interior of larger water bodies. The order of first appearance of clay mineral groups from shore to basin areas can be kaolinite, illite, chlorite, palygorskite, and sepiolite. In addition, montmorillonite and illite/smectite mixed layered minerals can settle in the whole range. During sedimentation, clay minerals can be neoformed via direct precipitation as well as aging of amorphous materials, inherited from weathered crusts via transportation, and transformed into different types in response to environmental reactions (Velde, 1995; Galán, 2006).

Sediments are reactive in not only original deposition sites but also burial sites. When sedimentary rocks are buried, owing to the removal of free or weakly-bonded water, the porosity would significantly shrink at the top layer of burial. The greater the burial depth the higher the ambient temperature. In sediments, clay minerals and other phases that are relatively stable when at the very surface of the earth become unstable at the elevated temperatures. The unstable phases tend to transform into new phases under the new environmental conditions, ultimately achieving a chemical equilibrium. The reactions are mostly clay-clay and clay-solution types, governed by, mainly, temperature and time. Illite is the most common diagenetic product, and there are also illite/smectite mixed layered minerals, chlorite/smectite mixed layered minerals, kaolinite, chlorite and zeolite being formed (Velde, 1995; Galán, 2006).

Hydrothermal alteration, typically by means of the intrusion of plutonic rocks, can also transform rock-forming minerals into clay minerals. It involves the interaction between aqueous solution and rock, and normally occurs at higher than 50 °C. In addition, it is
worth mentioning that hydrothermal alteration can produce pure kaolin (Velde, 1995; Galán, 2006).

### 3.4.3 Structures of clay minerals

Clay minerals are representative for the phyllosilicate group within the entire family of silicate minerals. There is a huge diversity in composition of clay minerals due to their large compositional ranges of solid solutions and their capability to form poly-phased crystals by interstratification (Meunier, 2005). The crystal structures that afford clay minerals such a compositional diversity will be introduced concisely in the following part of the section.

All types of clay minerals are structurally composed of tetrahedral sheets, octahedral sheets and, sometimes, inter-layer space occupants (water molecules and/or cations). Every single tetrahedron contains a cation (Si$^{4+}$, Al$^{3+}$ or Fe$^{3+}$), situated centrally and coordinated to four oxygen atoms as the four vertices. Each tetrahedron shares three vertices (i.e. the basal oxygen atoms) with three adjacent tetrahedra, forming an infinite two-dimensional network of pseudo-hexagonal rings in the x-y plane. The other vertex (i.e. the apical oxygen atom) is not used to connect adjacent tetrahedra, and all such vertices in a tetrahedral sheet point to a same direction (Brigatti, Galan & Theng, 2006). In each octahedron, there is also a cation situated centrally, and the cation is typically Al$^{3+}$, Fe$^{3+}$, Mg$^{2+}$, or Fe$^{2+}$. Oxygen atoms and hydroxyl ions normally form the six vertices, coordinated to the central cation. Neighbouring octahedra are linked by sharing edges. An illustration of typical structures of tetrahedra and octahedra is given in Figure 3.17 (slightly modified from Jordán, 2014).

All clay minerals are formed by stacking tetrahedral and octahedral sheets. The connection of two different types of sheets is achieved by allowing some of the octahedral vertices to share the tetrahedral apical oxygen atoms. In addition, the octahedral vertices uninvolved in the sheets connection are normally occupied by anions, such as oxygen atoms, hydroxyl ions, fluoride ions and chloride ions. These anions lie near to the centre of each tetrahedral 6-fold ring (Brigatti, Galan & Theng, 2006). It is worth mentioning that the cation-anion bonds in both types of sheets are intermediate between ionic and covalent bonds (Meunier, 2005). The most common layered structures of clay minerals are 1:1 structure, composed of the repetition of one tetrahedral sheet and one octahedral sheet, and 2:1 structure, where one octahedral
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sheet is sandwiched by two tetrahedral sheets, as shown in Figure 3.18 (modified from Brigatti, Galan & Theng, 2006).

Commonly, the unit cell of 1:1 structure is characterized by six octahedra and four tetrahedra, while that of 2:1 structure is characterized by six octahedra and eight tetrahedra. In a unit cell, if only two thirds of possible octahedral occupancies are taken, due to the presence of trivalent $\text{Al}^{3+}$ ions, the mineral is referred to as dioctahedral. In contrast, when all possible octahedral sites are occupied because of the presence of divalent $\text{Mg}^{2+}$ or $\text{Fe}^{2+}$ ions, the mineral is referred to as trioctahedral (Brigatti, Galan & Theng, 2006). Figure 3.19 shows the difference in structure between dioctahedral layer and trioctahedral layer (Wittke, 2014).

![Diagram of tetrahedral and octahedral sheets](image)
Clay minerals can be divided into the following groups: kaolin group, illite group, smectite group and chlorite group. The most typical minerals from each group are kaolinite, illite, montmorillonite and chlorite.
a) Kaolinite

Kaolinite is a typical member of kaolin group, having a chemical formula of $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$. The unit cell of kaolinite features a dioctahedral 1:1 layer structure, where each layer is composed of a repetitive stacking sequence of one tetrahedral sheet and one octahedral sheet, as exhibited in Figure 3.20 (Cheng et al, 2012). The H bond acts in between layers.

![Figure 3.20 The structure of kaolinite (Cheng et al, 2012)](image)

b) Illite

Illite is a typical dioctahedral 2:1 phyllosilicate representing illite group. The unit cell structure of illite resembles very much that of muscovite, where a sheet of octahedrally coordinated cations is sandwiched by two tetrahedral $\text{SiO}_4^{4-}$ sheets to form a layer. Since such 2:1 layers in illite exhibit a net negative charge, planes of K$^+$ ions are present in between every two layers to keep the whole structure electrically neutral. A general chemical formula of illite can be written as $K_y\text{Al}_4(\text{Si}_{8-y}\text{Al}_y)\text{O}_{20}(\text{OH})_4$, where $y$ is typically around 1.5, and therefore it can be learned that illite contains more Si but less K than muscovite (Deer, Howie & Zussman, 1992). The structure of illite is illustrated in Figure 3.21 (Murray, 2006).
Montmorillonite is a principal mineral of smectite group, featuring dioctahedral 2:1 layer structure, which is similar to that of illite. The ideal chemical formula of montmorillonite can be expressed as \((\text{Al}_{3.15}\text{Mg}_{0.85})\text{Si}_8\text{O}_{20}(\text{OH})_4\text{X}_{0.85}\cdot n\text{H}_2\text{O}\), where X is a monovalent interlayer cation (Newman, 1987). The 2:1 layer of montmorillonite is always negatively charged, due to the presence of octahedral divalent cations (i.e. Mg). On the other hand, the interlayer cations allow the whole structure of montmorillonite to achieve the balance in charge. It should also be noted that these interlayer cations are usually hydrated and exchangeable. Although the interlayer water can be easily removed by means of drying, the hydrated state can resume soon upon exposure to atmospheric temperature and humidity. Moreover, the thickness of interlayer space would increase as the absorption of water molecules continues, which means montmorillonite is expandable (Newman, 1987; Deer, Howie & Zussman, 1992). Figure 3.22 shows the structure of montmorillonite (Murray, 2006).

Figure 3.21 The structure of illite (Murray, 2006)
d) Chlorite

Chlorite is more often referred to as 2:1:1 clay mineral. It is composed of regularly alternating 2:1 tetrahedral-octahedral-tetrahedral layers, which are negatively charged, and octahedral brucite-like or gibbsite-like interlayer sheets, which are positively charged and present in between every two 2:1 layers (Deer, Howie & Zussman, 1992). The 2:1 layers can be either dioctahedral or trioctahedral, depending on the valence of the octahedral cations (tri-valent or di-valent), and so are octahedral interlayers (Brigatti, Galan & Theng, 2006). A typical chlorite structure is shown in Figure 3.23 (Murray, 2006).
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The general benefits of using SCMs in concrete have been extensively recognized by researchers and industries. Compared to the enormous manufacture scale of Portland cement, traditional SCMs, such as PFA, GGBS and silica fume, are still produced in a significantly less quantity worldwide. This leads to the imbalance of traditional SCMs between the limited availability and the high demand. In the UK, this issue has been particularly pronounced and prevalent, mainly due to biomass and gas increasingly becoming the preferred resources, instead of coal, for coal-fired power plants. Alternative sources of SCM are therefore of large interest to cement and concrete industries.

As a common product of diverse geological activities, clay is in excellent availability worldwide. Generally, it can become an alternative SCM upon calcining at appropriate

Figure 3.23 The structure of chlorite (Murray, 2006)

3.4.4 The use of calcined clay as a SCM

The general benefits of using SCMs in concrete have been extensively recognized by researchers and industries. Compared to the enormous manufacture scale of Portland cement, traditional SCMs, such as PFA, GGBS and silica fume, are still produced in a significantly less quantity worldwide. This leads to the imbalance of traditional SCMs between the limited availability and the high demand. In the UK, this issue has been particularly pronounced and prevalent, mainly due to biomass and gas increasingly becoming the preferred resources, instead of coal, for coal-fired power plants. Alternative sources of SCM are therefore of large interest to cement and concrete industries.

As a common product of diverse geological activities, clay is in excellent availability worldwide. Generally, it can become an alternative SCM upon calcining at appropriate

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temperatures, which are usually much lower than that required for manufacturing cement clinker (around 1500 °C). Clay minerals would suffer a structural disorder from the calcining process by, mainly, losing octahedral hydroxyl ions. This transforms clay minerals from a crystalline state into an amorphous state, in which they become much more exposed and vulnerable to the attack of alkalis. Calcined clay can therefore participate in pozzolanic reaction, in which various amorphous phases of calcined clay react with calcium hydroxide in the presence of water to form a range of cementing products. As an example, the pozzolanic reaction of calcined kaolinite (i.e. metakaolin) can form C-S-H gel, C_2ASH_8 (strätlingite), C_3ASH_6 (hydrogarnet) and C_4AH_{13} (Murat, 1983). It is worth noticing that clay minerals can differ from each other in the temperature and the process of the crystalline-to-amorphous structural transformation by calcining, which is because of their structural diversity and will be discussed in detail in the following chapters. The mineralogical compositions of clay can vary substantially across different regions. In addition to clay minerals, some clays may contain a high content of non-clay impurities, such as quartz and feldspar, which are unfavourable to the pozzolanic reactivity of calcined clays. As mentioned in the genesis of clay, pure clays can form underneath the surface of the earth by hydrothermal alteration but they are usually unavailable due to the inaccessibility. Moreover, on the other hand, the technology to purify the clays with a high content of impurities is complex and expensive (Tironi et al, 2012). This is considered as a shortcoming of using calcined clay as a SCM.

3.4.4 a) Metakaolin

In most of the preceding SCM-related studies, the term ‘calcined clay’ very often refers to metakaolin. Sabir, Wild & Bai (2001) concluded that metakaolin is an excellent pozzolan, and the addition of metakaolin can alter the pore structures of cement paste, mortar and concrete, improving the strengths of concrete at both early and late ages. Siddique & Klaus (2009) concluded the advantages of using metakaolin as a SCM in concrete, which included increased compressive and flexural strengths, reduced permeability, increased resistance to chemical attack; increased durability, reduced effects of alkali-silica reactivity, enhanced workability and finishing of concrete, and reduced shrinkage due to particle packing. Similar findings were reported in many other works. For instance, Zhang & Malhotra (1995) showed that the concrete with 10 wt.% of Portland cement substituted by metakaolin achieved higher compressive
strength at various ages (up to 180 days) than the control concrete, and, in comparison with the concrete containing silica fume at the same cement replacement level, it was still superior at early ages, in terms of compressive strength. Wild, Khatib & Jones (1996) found that the concrete containing metakaolin gained enhanced long term strength, as compared to the control concrete, and the maximum enhancement was achieved at the Portland cement replacement level of 20 wt.%. Curcio, DeAngelis & Pagliolico (1998) examined four different commercially available metakaolins, in terms of the effect on improving the compressive strength development of super-plasticized mortars. They found that, at a cement replacement level of 15 wt.% and a w/b ratio of 0.33, metakaolins were more effective than silica fume on enhancing the compressive strength of mortar before 28 days. At relatively late ages (i.e. 90 and 180 days), the compressive strengths of mortars incorporating metakaolins and silica fume were similar. Badogiannis et al (2004, 2005) stated that the metakaolin produced from a poor Greek kaolin can improve the strength of concrete when it was used to replace Portland cement content (10 and 20 wt.%). Kim, Lee & Moon (2007) reported that the concrete where 15 wt.% of Portland cement content was substituted by a Korean local metakaolin at a w/b ratio of 0.25 exhibited impressive improvement in compressive, tensile and flexural strengths at various ages. Said-Mansour et al (2011) stated that the addition of metakaolin to substitute 10 wt.% of Portland cement is beneficial to the mechanical properties of mortars, and the resistance of mortars to acid attack can be improved as well. Ramezanianpour & Bahrami Jovein (2012) examined the concrete specimens incorporating the metakaolin produced from an Iranian local clay with high kaolinite content, in terms of compressive strength and durability. The results suggested that the replacement of Portland cement by the metakaolin improved the compressive strengths of concrete at various ages (up to 180 days), and the optimum replacement levels were found to be 12.5 wt.% for the w/b ratio 0.4 and 10 wt.% for the w/b ratio 0.5. The durability of the concrete was also enhanced due to the incorporation of metakaolin. Furthermore, Gruber et al (2001) reported that the incorporation of high-reactivity metakaolin (8 and 12 wt.%), produced from a purified kaolinic clay, can considerably enhance the resistance to chloride ion diffusion for concrete. In the work by Courard et al (2003) on the durability of mortars containing metakaolin, the resistance to chloride diffusion and sulphate attack was significantly improved for the mortars with 10 and 15 wt.% of Portland cement content being substituted by metakaolin.
3.4.4 b) Calcined illite and calcined montmorillonite

Metakaolin is a well-known SCM, but the clay minerals other than kaolinite, such as illite and montmorillonite, have not been extensively investigated in terms of the pozzolanic reactivity and the effect on improving the properties of concrete. He, Makovicky & Øsbæk (1995) examined the pozzolanic reactivity of illite calcined at 650, 790 and 930 °C, and they concluded that calcined illite has very low pozzolanic reactivity. In their work, the mortar with 20 wt.% calcined illite exhibited only 79% of the compressive strength of the control mortar after 28 days. Fernandez, Martirena & Scrivener (2011) confirmed the low pozzolanic reactivity of calcined illite.

The pozzolanic reactivity of calcined montmorillonite was studied by He, Makovicky & Øsbæk (1996). They suggested that the montmorillonite calcined at 830 °C is fairly pozzolanic. Fernandez, Martirena & Scrivener (2011) conducted a similar investigation, and further stated that calcined montmorillonite has higher pozzolanic reactivity than calcined illite but lower than calcined kaolinite (i.e. metakaolin).

3.4.4 c) Calcined clay brick

Industrial waste calcined clay bricks and tiles have been worldwide investigated to partially replace Portland cement content in mortar and concrete. However, the firing temperature used to produce bricks from clay considerably varies case by case (800 °C ~ above 1000 °C). O’Farrell, Wild & Sabir (2001) examined ground calcined clay bricks from four different European countries, and they found that the partial substitution of Portland cement by the ground calcined clay brick with higher glass content can improve the pore size distribution and compressive strength of the mortars. Negative results were also observed for the ground bricks with low glass content. O’Farrell, Sabir & Wild (2006) studied a waste clay brick calcined at 1000 °C, and they observed that the addition of waste ground clay brick led to a drop in compressive strengths of the mortars at early ages, as compared to those of the control mortar. At the late age (i.e. 90 days), replacement levels of up to 20 wt.% resulted in the strengths equivalent to or higher than that of the control mortar. Toledo Filho et al (2007) investigated a ground calcined clay brick, produced at 850 °C in Brazil and used to replace 10, 20, 30 and 40 wt.% of Portland cement in mortars. They stated that the addition of ground calcined clay brick at up to 20 wt.% level did not result in any adverse effect on the compressive strength and elastic modulus of mortars at various
ages, and, moreover, the sorptivity of mortars was reduced, due to the refined pore structure. Naceri & Hamina (2009) employed an Algerian ground clay brick, fired at below 900 °C, as a substitution (5, 10, 15 and 20 wt.%) for Portland cement in mortars. At the replacement level of 5 and 10 wt.%, the compressive and flexural strengths of mortars were determined to be higher than those of control mortar at 90 days. They therefore suggested that the Algerian waste brick can be used to replace up to 10 wt.% of Portland cement content in the manufacture of mortar. Vejmelková et al (2012) conducted a comparison between the high performance concrete (HPC) incorporating 10 wt.% of a Czechic waste ground clay brick as SCM and another HPC containing 10 wt.% of a Czechic metakaolin. Their results showed that the compressive strength of the former HPC was marginally lower than the latter at all ages, however, the effective fracture toughness, specific fracture energy and the loss of mass in the de-icing salt resistance were slightly superior.

3.4.4 d) LC3 cement

In recent years, a new ternary blend of limestone, calcined clay and clinker, called LC3 cement, has arisen, with industrial trials already being implemented in Cuba (Berriel et al, 2016). It essentially involves a partial substitution for clinker content by limestone and metakaolin. The chemistry underlying the hydration of this LC3 cement is that limestone reacts with C₃A content of clinker and aluminate content of metakaolin, in the presence of water and calcium hydroxide, to form calcium hemicarboaluminate hydrate and calcium monocarboaluminate hydrate. In addition, there is less calcium monosulfoaluminate hydrate (AFm phase) formed, leading to a stabilization of ettringite, which is the main contributor to early strength. Antoni et al (2012) reported that a substitution of 45% clinker content by 30% metakaolin and 15% limestone resulted in improved mechanical properties on both 7 and 28-day, as compared to the 100% Portland cement reference.

3.4.4 e) Calcining temperature

Temperature is the key parameter in the calcining process. There appear to be significant inconsistency in the optimum calcining temperature used to produce metakaolin from kaolin. The term ‘optimum calcining temperature’ refers to the temperature at which clay or clay mineral is calcined to exhibit its highest pozzolanic reactivity. Ambroise, Murat & Pera (1986) stated that the calcining temperature to
produce active metakaolin phase should be within the range of 600–800 °C. Sayanam et al. (1989) suggested that metakaolin with high reactivity can be obtained by calcining kaolin at 600–900 °C. Shvarzaman et al. (2003) believes that a complete dehydroxylation and transformation of kaolinite to metakaolin can be achieved at 570–700 °C. However, Mejia de Gutiérrez et al. (2006) demonstrates the optimum calcining temperature of producing metakaolin from kaolin is between 700 and 800 °C. Rashad (2013) reviewed more than two hundred relevant works, and stated that the ‘optimum’ calcining temperatures proposed by those researchers ranged from 600 to 900 °C, and the calcining periods were within 1 to 24 hours. It should be noted that almost all of these clays can refer to kaolinitic clays, whose dominant constituent was kaolinite. In the case of non-kaolinitic clays (low or no kaolinite content, high impurities content, no absolutely dominant mineral phase, etc.), the situation would be far more complicated in terms of optimum calcining temperatures. This is because, for different clay minerals, the collapse of crystal lattice structure (i.e. the crystalline-to-amorphous structural transformation) occurs at different temperatures. Hé, Makovicky & Osbaeck (1994, 1995, 1996) suggested that the optimum calcining temperatures of high-purity kaolinite, illite and Ca-/Na- montmorillonite were examined to be 650 °C, 930 °C and 830 °C, respectively. Tironi et al. (2013) further stated that 550–900 °C can lead to the dehydroxylation of argillaceous minerals and the subsequent formation of amorphous aluminosilicate phases without causing recrystallization of mullite. It is therefore clear that the optimum calcining temperature of a certain type of clay is largely dependent on its mineralogical and chemical compositions.

For the clays with complicated mineralogical compositions, such as London clay in this study, when determining the optimum calcining temperature, it is crucial to understand how each crystalline phase would respond, chemically and structurally, to increasingly intensive heat. There have been only a limited number of studies so far, focusing on the technical viability of using such complex clays as SCM in concrete. Chakchouk, Samet & Mnif (2006) investigated Tunisian clay samples collected from five different sites, in terms of the potential use as pozzolanic material. Danner (2013) examined the pozzolanic reactivity of calcined clays, which were collected from Denmark, Poland and Portugal. Regarding London clay, there has been no relevant work reporting its potential to act as a SCM in concrete after calcining. That is exactly the scientific
contribution of this study and this thesis. The genesis and formation of London clay is introduced in the following section.

**3.4.5 London clay**

London clay has unique geological and mineralogical properties. It was described by British Geological Survey (2012) as ‘the London clay mainly comprises bioturbated or poorly laminated, blue-grey or grey-brown, slightly calcareous, silty to very silty clay, clayey silt and sometimes silt, with some layers of sandy clay.’ British Geological Survey (2012) also added that ‘London clay commonly contains thin courses of carbonate concretions (cementstone nodules) and disseminated pyrite, and it also includes a few thin beds of shells and fine sand partings or pockets of sand, which commonly increase towards the base and towards the top of the formation.’

London clay was formed due to a sequence of deposition-erosion events (Gasparre, 2005). King (1981) suggested that the deposition of London clay commenced in the Early Eocene (~50 million years ago), and it was caused by a rise of sea level over part of Southern England up to the Welsh Massif, Northern France, Western and Northern Belgium and Northern Germany. In the London Basin, the London Clay Formation lies above the Harwich Formation, which is a glauconitic sand and was the first material deposited into the embryonic sea, and below the Virginia Water Formation, which is a bioturbated glauconitic sand (King, 1981). The total thickness of the London Clay Formation in the London Basin is 50~150m, and it decreases westwards (King, 1991). Apart from the deposition process, the formation of London clay was also influenced by the Alpine orogeny, erosion and weathering (King, 1981). The erosion happened to all the overlying deposits in the Tertiary and Pleistocene epochs, resulting in mechanical overconsolidation of London clay (King, 1981). That was followed by weathering.

In terms of clay minerals, London clay is comprised of poorly crystalline kaolinite, chlorite, illite and smectite (Gasparre, 2005). Furthermore, it was suggested that the mineralogical compositions of London clay can vary across the London Basin (Gasparre, 2005). Kaolinite and illite can be predominant in the west and east of the London Basin, respectively. The clay in central London can be compositionally governed by smectite and illite. The London clay studied in this work was excavated from Pudding Mill Lane, which is very close to central London area. As confirmed by
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colorization, it is predominantly composed of montmorillonite (a type of smectite). Details about this can be found in Chapter 5.
3.5 Crossrail

Crossrail is a London transport project, a new 118-kilometre-long railway line starting from Heathrow and Reading in the west to Abbey Wood and Shenfield in the east, as shown in Figure 3.24 (Pickard, 2014). The construction works commenced in 2009, and all services are due to open to the public in 2019. This project involves the construction of new railway tunnels, which are 6.2 metres wide as the internal diameter, 40 metres deep from the ground and 42 kilometres long in total, as well as a further 14 kilometres of stations and interchange tunnels (Crossrail, 2013). Eight tunnel boring machines (TBMs), each of which has a weight of around 1000 tonnes, an external diameter of 7.1 metres and a length of around 150 metres, were employed to dig the new tunnels on a 24-hour-a-day and 7-day-a-week basis (Crossrail, 2015b). Figure 3.25 provides an impression of the excavated tunnel (Crossrail, 2015c), and Figure 3.26 shows the TBM (Crossrail, 2015b).

![Figure 3.24 The route map of Crossrail (Pickard, 2014)]
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Figure 3.25 The excavated tunnel of Crossrail (Crossrail, 2015c)

Figure 3.26 A tunnel boring machine used in Crossrail (Crossrail, 2015b)
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It was reported that the tunnelling work of Crossrail produced around 7 million tonnes of excavated London clay, 98% of which has been reused in various applications. For example, about 3 million tonnes was used to construct an artificial wetland nature reserve in Wallasea Island, in Essex. Other applications included land raising in Kingsworth, golf course in Ingrebourne, grazing pasture for livestock in Goshems Farm, and landfill restoration in Ockendon, Rainham and Calvert (Crossrail, 2015a).

Those applications did not achieve the best value of excavated London clay, as they were basically nothing more than a geographic displacement of clay. In contrast, developing excavated London clay into a SCM would be a higher value reuse, which can result in both environmental and economic benefits.

This chapter has provided the necessary background information about the research, covering Portland cement, concrete, SCM, clay and Crossrail, and emphasised the potential of using calcined London clay as a SCM in concrete. The next chapter is focused on introducing the materials and methods used in this study.
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4.1 Materials

4.4.1 Portland cement

CEM-I 42.5 N conforming to BS EN 197-1 (Hope Construction Materials, UK) was used in paste, mortar and concrete. The chemical composition of this CEM-I is given in Table 5.1. The mineralogical composition calculated using Bogue’s equation was 61.5 wt.% C$_3$S, 13.8 wt.% C$_2$S, 7.1 wt.% C$_3$A and 8.2 wt.% C$_4$AF.

4.4.2 Aggregates

Thames Valley gravel (Travis Perkins, UK) with a specific gravity of 2.42 and particle fineness between 5 and 14 mm was used as coarse aggregate. The natural moisture content and 24-hour water absorption were measured to be 0.49% and 3.06%, respectively. Silica sand (Travis Perkins, UK) with particle fineness less than 5 mm was used as fine aggregate. It had a specific gravity of 2.58, a moisture content of 0.44%, and a water absorption of 0.63%. The measurement of natural moisture content and water absorption for aggregates was in compliance with ASTM C127-15 and ASTM C128-15.

4.4.3 London clay

London clay was directly supplied by Crossrail, from the tunnelling site near Pudding Mill Lane in East London. The London clay is a lower Eocene sediment (Ypresian in age) and is one of a sequence in the London basin that extends from Wiltshire in the west, to Essex in the north east and Kent in the south east. It is largely covered with younger (Miocene, Pliocene and Quaternary) sediments, although it is exposed to both north and south of the Thames. The characterization of London clay follows in Chapter 5.

4.4.4 PFA

PFA was supplied by Lafarge Tarmac. It had a median particle size of 15.3 µm, and a measured true density of 2.4 g/cm$^3$. Detailed characterization of PFA is included in Chapter 5.
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4.4.5 GGBS

GGBS was provided by Lafarge Tarmac. The median particle size was measured to be 16.1 µm, and the true density was measured to be 3.1 g/cm$^3$. The characterization of GGBS is included in Chapter 5.

4.4.6 Silica fume

Silica fume was supplied in condensed form by Lafarge Tarmac. The median particle sizes before and after sonication were 116.2 and 6.9 µm, respectively. The true density was determined to be 2.4 g/cm$^3$. Detailed characterization of silica fume follows in Chapter 5.
4.2 Methods

4.2.1 Calcining excavated London clay

The excavated London clay was directly supplied from one of the tunnelling sites of Crossrail and safely contained in plastic tubs. The original moisture within the raw clay was determined to be around 30 wt.%. The raw clay was manually formed into lumps having irregular shapes and then dried in an oven at a temperature of 105 °C for 24 hours. All the dried raw clay lumps were ground to a fine powder using a vibratory disc mill (Gy-Ro, Glen Creston Ltd, UK) for 1 minute. The clay powder will be called the as-received clay throughout the rest of this thesis. The as-received clay sample was subsequently calcined in alumina crucibles at 600 °C, 700 °C, 800 °C, 850 °C, 900 °C, 950 °C and 1000 °C using a 2-hour dwell in an electric chamber furnace (Carbolite, UK). As soon as the fixed dwell time finished, samples were removed from furnace immediately and allowed to cool to the ambient temperature in the air.

4.2.2 Grinding calcined clay

All the calcined clay samples were re-ground in the same vibratory disc mill (Gy-Ro, Glen Creston Ltd, UK) to attain a consistent particle fineness. A milling time of 2 minutes was selected because laser diffraction analysis showed that further grinding could not cause any further significant reduction in particle size.
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4.2.3 Analytical techniques

A range of analytical techniques were employed to characterize as-received London clay, ground calcined clay and other materials, including GGBS, PFA and silica fume.

a) X-Ray Fluorescence Analysis (XRF)

X-ray fluorescence (XRF) analysis was conducted to investigate the chemical composition of as-received London clay sample. The principles behind this technique can be briefly explained as follows. When high energy X-rays are emitted to an atom, they could make it unstable by ejecting an electron from its inner orbit. The electrons that lie in outer orbits and possess higher energy may fall into the inner orbit to fill the space left by the removed electron. As a result of the migration of the electron between two orbits, energy is released as a secondary X-ray. The energy is quantitatively equivalent to the energy difference of the two involved orbits, and the secondary X-ray is characteristic to the element. By recording characteristic wavelengths and intensities of secondary X-ray radiations from a sample, an XRF analyser is capable of doing not only qualitative but also quantitative composition analysis.

In this study, a wavelength dispersive X-ray fluorescence spectrometer (Bruker AXS S4 explorer) was used for the elemental investigation. The elements it can measure is ranging from Na$^{11}$ to U$^{92}$, in the atomic number order.

b) Density Measurement

Raw London clay underwent a range of mechanical and thermal treatment, involving drying, shaping, grinding, calcining, cooling and re-grinding, which makes it not only pozzolanic but resembling ordinary Portland cement in shape. Understanding the density of calcined clay in the fine powder form is significant when designing the mix proportion of concrete incorporating calcined London clay. Details can be found in the later chapter.

The density measuring technique used in this study is gas pycnometry. In a gas pycnometer, the sample is first placed in a sample chamber with known internal volume, and an inert gas is then introduced to pressurize the sample chamber. After the equilibrium is reached in the first chamber, the gas is freed to a second empty chamber, whose internal volume is also known. Finally, another pressure equilibrium is reached within the system, which is composed of two chambers and a pathway.
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connecting both. The internal volumes of both chambers and the pressures of both equilibriums allow the calculation for the volume of the powder sample, which is as follows (Lowell et al, 2012):

\[
V = V_1 + \frac{V_2}{1 - \frac{P_1}{P_2}}
\]

where \( V \) is the volume of the sample, \( V_1 \) is the internal volume of the first chamber when empty, \( V_2 \) is the internal volume of the second chamber when empty, \( P_1 \) is the pressure under the first equilibrium, and \( P_2 \) is the pressure under the second equilibrium. The absolute density (true density) of any powder sample can be subsequently obtained as the ratio of the mass to the measured volume.

The gas displacement pycnometer used in this study is a Micromeritics AccuPyc 1330. Each powder sample was purged with helium 10 times in the sample chamber to remove surface moisture on the particles before each measurement began. The reported result for each measurement is the average of 10 runs.

c) Particle Size Distribution by Laser Diffraction

As emphasized previously, particle fineness is considered as a critical factor that can affect how SCMs effectively work in a cement matrix. Determining particle size distribution of ground calcined London clay is indispensable, and laser diffraction spectroscopy is employed for the measurement. The laser diffraction particle size analyser used in this research was a Coulter LS 100, which can analyse particles with a dimension ranging from 0.4 to 900 µm. All the materials involved in the study, including as-received clay, calcined clay, PFA, GGBS and silica fume, were tested by the machine. Ultrasound was used to facilitate the dispersion of powders in the water within the sample vessel, which is particularly important for analysing densified silica fume.

d) Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) technique was employed to examine the morphology of all the ground London clay samples. Investigating the morphology of particles is significantly important, as it may help understand the workability of concrete incorporating the particles as a supplementary cementitious material.
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Pulverised fuel ash (PFA), for example, can improve the workability of concrete due to its spherical shape. SEM can also provide information, as a complementary method to XRD and FTIR, to qualitative analyse minerals in the London clay. This is because some minerals have particular shapes, which can be easily identified in SEM images. SEM investigation was also applied to the cement pastes containing calcined London clay.

The scanning electron microscope used in this study was a JEOL JSM-5610LV fitted with a secondary electron detector (Massachusetts, USA). The powder samples including PFA, GGBS, silica fume, as-received and calcined London clay were stuck and spread on a number of specimen stubs. A thin layer of gold was used to coat each stub and make the sample conductive. All the samples were subsequently examined in the SEM under the secondary electron mode with an accelerating voltage of 15 kV.

e) X-Ray Diffraction Analysis (XRD)

XRD was utilised to analyse crystalline phases and amorphous phases within the as-received London clay sample as well as the calcined clay samples. It is an accessible and useful technique for identifying single crystalline phases in a polyphase system. The principle behind it can be briefly explained as follows. When a monochromatic beam of X-ray is directed at a sample, the incident ray would be diffracted, producing constructive interference under certain circumstances. More specifically, the constructive interference of diffracted ray can take place only when a certain incident angle, the wavelength of electromagnetic radiation and a lattice spacing between two diffracted planes satisfy Bragg's Law ($2d\sin\theta = n\lambda$). By examining the sample through a range of pre-determined incident angles, all the diffraction information of the lattice can be collected for analysis. The identification of crystalline minerals can be realised after the conversion of diffraction peaks to d-spacings (Integrating Research and Education, 2015).

To analyse clays and identify clay minerals on XRD requires considerable experiences, because clays are mostly poly-phase systems and complicated in mineralogical compositions. In order to study the exact mineralogy of a certain clay, a diverse range of pre-treatments for the clay sample are normally needed to refine clay particles and remove unfavourable substances that can cause difficulties to identify clay minerals on diffractograms. As an example of those kinds of substances, iron oxides can
produce a high background on diffractograms, which could possibly overlap and mask peaks corresponding to clay minerals (Moore & Reynolds, 1997). This is due to the secondary X-ray deriving from the interaction between iron and the incident X-ray. The mentioned pre-treatments usually include clay mineral separation, decantation, centrifugation, ultrasonic disaggregation and chemical treatment.

In many cases, the orientation of clay minerals is another important factor influencing the quality of a diffractogram. Each clay mineral has distinctive 00l reflections on the diffractogram, which makes such a clay mineral easily recognizable. This is because the atomic pattern along z-axis varies greatly between clay minerals. However, the intensities of 00l peaks are sometimes too weak and it is therefore difficult to differentiate a 00l peak from another or the background. Different sample preparation methods have been suggested and used to make oriented clay samples, which can effectively increase the intensities of 00l peaks and consequently facilitate the observation of 00l reflexes. In some cases, it is necessary to examine a full range of reflections rather than only 00l for clay minerals. For example, the 060 peak is significant in identifying di-octahedral and tri-octahedral species (Moore & Reynolds, 1997). All reflections can be observed only on a randomly oriented clay sample.

In this study, the as-received London clay sample and all calcined clay samples were examined on a PANalytical X'Pert Pro MPD diffractometer (Philips, Netherland) equipped with a detector. The radiation was Cu-Kα with a wavelength of 1.54060 Å. All measurements were taken from 5 to 70 °2θ using a step size of 0.0334 °2θ and a step time of 105 seconds with an accelerating voltage of 40 kV. The subsequent phase identification was completed on X'Pert HighScore Plus software from PANalytical by comparing experimental data with standard patterns from the ICDD reference database.

f) Fourier Transformed Infrared Spectroscopy (FTIR)

Fourier Transformed Infrared Spectroscopy (FTIR) technique was used in this study, together with XRD, to investigate the mineralogy of excavated London clay. A molecule can absorb radiation only at certain frequencies, which must match the frequencies the molecule itself vibrates at. This fact suggests that a molecule has its own characteristic wavelengths (or frequencies) in infrared adsorption spectroscopy. An unknown substance therefore can be qualitatively analysed by understanding its
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IR spectrum. This is mainly because, compared to XRD, an IR spectrum contains some more detailed information on amorphous phases.

All the as-received and calcined clay samples were examined on a Thermo Scientific Nicolet 6700 spectrometer equipped with an IR source, KBr beam splitter and DTGS KBr detector. A Quest Single Reflection Attenuated Total Reflectance (ATR) accessory was used to directly test all the samples, instead of using the potassium bromide pressed-disc technique. 200 scans in the 500 ~ 4000 cm\(^{-1}\) spectral range with a resolution of 2 cm\(^{-1}\) were taken on each sample.

In the FTIR system, a beam containing the full spectrum of frequencies is emitted from an IR source. Before the beam reaches samples, it must enter an interferometer, where the original beam is divided into two beams by a beam splitter and the two beams get interfered with each other by a certain configuration of mirrors. The resulting beam from the interferometer is then directly transmitted to the sample compartment, and the light at particular wavelengths is absorbed by samples. A detector is used to collect the light leaving the sample compartment, measure its intensity and produce the raw data ready to be processed in the computer by the Fourier transformation.

**g) Thermal Analysis**

Thermogravimetric analysis (TGA) was carried out to investigate the dehydroxylation phenomenon of the clay minerals within the as-received London clay sample. As mentioned previously, the temperatures that trigger the dehydroxylation of different clay minerals vary, which is due to the diversity of microstructure of clay minerals. TGA can provide the information about the weight loss of a sample in consecutive temperature intervals. By interpreting TGA data, it is possible to characterize the types of clay minerals and obtain a rough estimation of their amounts within the sample.

The measurement for both as-received and calcined London clay was performed with a Polymer Laboratories Thermal Science STA 1500 analyser, and the temperature was raised from 30 °C to 1000 °C with a heating rate of 15 °C/min. A nitrogen atmosphere with a flow rate of 50 ml/min was kept in the heating chamber, in order to avoid carbonation of the sample.
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h) Inductively coupled plasma optical emission spectroscopy (ICP-OES)

ICP-OES technique was applied to measure the ion release of as-received and calcined clay samples into solutions. Comparing the results of different samples can help better understand the microstructural changes thermal activation caused to the minerals in the clay. A range of elements have been examined in the ICP-OES analysis. Si and Al are of particular importance, as they are the main elements undergoing pozzolanic reaction to form C-S-H, C-A-H and C-A-S-H phases.

2 g of clay sample was mixed with 100 ml of distilled water in a plastic bottle. For the same sample, three specimen bottles were prepared so that an average test result of three can be obtained. All the bottles were firmly capped and continuously rotated on a bottle roller for 7 days. A week later, for every bottle, about 15 ml of solution was transferred to an ICP test cube. Before all the tubes were taken for analysis, a high speed centrifuge was used to sediment suspended clay particles from the clear solutions in the tubes. Moreover, a reference solution containing only distilled water was prepared by the same manner. The ICP-OES used in this experiment is a Perkin Elmer Optima 7000 DV spectrometer (Massachusetts, USA).

In the ICP-OES system, a sample is pumped into an analytical nebulizer, from which it is broken up into aerosol droplets. As soon as the aerosol droplets are subsequently introduced to argon plasma flame, a collision between the charged particles in the plasma and the sample takes place, which causes dissociation of molecules and ionization of atoms to the sample. Detectable radiation at different wavelengths is discharged as a result of this collision and each wavelength is characteristic for a specific element involved in the sample. In the optical chamber of the system, the emitted light is separated into different characteristic wavelengths, and then the intensity of light is measured as an indication of the element concentrations.

i) Specific Surface Area Measurement (BET Method)

It is understood that particle fineness of SCMs has a crucial impact on the porosity of the cement matrix and hence influences the mechanical and durability properties of the concrete. Investigating the particle fineness of ground calcined London clay is of critical importance in this study. Specific surface area, together with particle size
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distribution, is usually used to characterize the particle fineness of powders. It can be measured by applying gas adsorption technique and using BET isotherm.

A Micromeritics TriStar 3000 surface area and porosity analyser was used in this work. It is capable of measuring three samples simultaneously and providing data including surface area, pore volume and pore size distribution. Nitrogen gas and liquid nitrogen were adopted as adsorbate and cryogen, respectively. All the materials involved in this study were analysed to obtain specific surface area and porosity data. Overnight degassing at 105°C was performed to all the samples to remove moisture and adsorbed contaminants before starting gas adsorption.

j) Isothermal Conduction Calorimetry

Isothermal conduction calorimetry is a commonly used technique for studying the heat evolution of cement hydration. An isothermal conduction calorimeter can measure the amount of heat generated and released during cement hydration at a constant set temperature. In a modern instrument design, it normally comprises a sample chamber, a reference chamber, a common heat sink and two Peltier sensors that connect the heat sink to the sample chamber and the reference chamber, respectively. For a measurement, a sample ampoule containing prepared reactants is fitted into the sample chamber while a reference ampoule containing only inert quartz sand is inserted to the reference chamber. The two Peltier sensors are highly sensitive to the heat released from both ampoules, and capable of transforming the heat energy into electric voltage by thermoelectric effect. The difference between the two electric voltages from the sample ampoule sensor and the reference ampoule sensor is continuously recorded and computed to calorimetric signal.

In this study, a TAM Air isothermal 8-channel calorimeter (TA instruments, US) was used for all measurements. It is equipped with eight channels, each of which consists of a sample chamber and a reference chamber, and therefore eight samples can be tested simultaneously. The operating temperature for all measurements was set as 20 ± 0.02 °C. In addition to a control cement paste at a w/b ratio of 0.5, a range of pastes where 50% of CEM-I was replaced by different test materials were prepared with the same w/b ratio and measured for 48 hours. For each paste, a one-minute-long mixing of powders in dry state was done by hand in a beaker, followed by a quick mixing with added water for less than one minute. The paste was then poured into a plastic sample
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ampoule, and the ampoule was transferred into the calorimeter sample chamber immediately.
4.2.4 Assessment of pozzolanic reactivity

a) Frattini test

Frattini test has been widely used by researchers to study various pozzolans, such as metakaolin, catalytic cracking residues and PFA (Talero, 2005; Paya, Monzo & Borrachero, 2001; Rahhal & Talero, 2004). It is considered as one of direct methods for assessing pozzolanic reactivity, because it measures the concentration of Ca(OH)$_2$ straight from a prepared aqueous sample rather than measures a physical property of a test sample that indicates the degree of pozzolanic reactivity (Donatello, Tyrer & Cheeseman, 2010). Specifically, it involves chemical titrations to determine the concentrations of Ca$^{2+}$ ion and OH$^-$ ion in a solution made by mixing CEM-I and pozzolan with water.

Frattini test procedures specified in EN 196-5 were followed in this study. Each test sample was prepared by mixing 16 g of CEM-I and 4 g of test pozzolan with 100 ml of distilled water. The mix proportions can be found in Table 4.1. Test samples were all sealed in plastic vials with cling film and caps, and stored in an oven at 40 °C until the test times. After 8 days, samples were vacuum filtered using a filter paper with a nominal pore size of 2.7 µm (Whatman 542), and filtrates were allowed to cool to room temperature prior to subsequent titrations. Prepared 0.1 mol/l hydrochloric acid was used to titrate against filtrates to determine the concentrations of OH$^-$, with methyl orange being used as the indicator. Following the pH adjustment to 12.5 ± 0.2 by modestly adding NaOH solution into titrated filtrates, 0.03 mol/l EDTA solution and Patton and Reeder’s indicator were used in secondary titrations to determine the concentration of Ca$^{2+}$ in the filtrate. After one more week, a set of 15-day Frattini test data was collected in the same manner. All calcined clays were tested to assess pozzolanic reactivity, and GGBS, PFA, silica fume and inert silica sand were also tested to draw comparisons. Moreover, control sample that contains 20 g of CEM-I and no pozzolan addition was prepared and tested.
Table 4.1 The mix proportions for Frattini test

<table>
<thead>
<tr>
<th>Pastes</th>
<th>Test materials</th>
<th>CEM-I (g)</th>
<th>Water (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>4</td>
<td>16</td>
<td>100</td>
</tr>
<tr>
<td>600 °C CLC</td>
<td>4</td>
<td>16</td>
<td>100</td>
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<tr>
<td>700 °C CLC</td>
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<td>16</td>
<td>100</td>
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<td>800 °C CLC</td>
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<td>GGBS</td>
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<td>PFA</td>
<td>4</td>
<td>16</td>
<td>100</td>
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<tr>
<td>Silica fume</td>
<td>4</td>
<td>16</td>
<td>100</td>
</tr>
<tr>
<td>Ground sand</td>
<td>4</td>
<td>16</td>
<td>100</td>
</tr>
</tbody>
</table>

- CLC = calcined London clay

The Frattini test data is presented as CaO, equivalent to Ca$^{2+}$, in mmol/l on the y-axis against OH$^{-}$ in mmol/l on the x-axis. The solubility curve of lime at 40 °C is plotted, because it is a key component in the analysis to interpret test results. It defines the boundary on the graph between the pozzolanic area and the non-pozzolanic area.

b) Strength Activity Index (SAI) test

SAI test essentially measures and adopts compressive strengths of mortars, as an indicator, to present the extent of pozzolanic reactivity. Compressive strength test has been applied by a number of researchers to investigate pozzolanic reactivity of various materials, such as catalytic cracking residues, coal bottom ash, crashed bricks, glass powder, silica fume and sewage sludge ash (Tseng, Huang & Hsu, 2005; Cheriaf, Rocha & Pera, 1999; Wild, Khatib & O’Farrell, 1997; Shi et al, 2005; Mostafa et al, 2001; Agarwal, 2006; Monzo et al, 1999; Pan et al, 2003).

The procedures specified in BS 3892 were followed to carry out SAI test in this study. Calcined clays, GGBS, PFA, silica fume and ground silica sand were all tested and the mix proportions of mortar are listed in Table 4.2. A cement replacement level of 20 % was selected for all the materials.
Table 4.2 The mix proportions of mortars for SAI test

<table>
<thead>
<tr>
<th>Mortar mix</th>
<th>Test materials (g)</th>
<th>CEM-I (g)</th>
<th>Sand (g)</th>
<th>Water (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>-</td>
<td>450</td>
<td>1350</td>
<td>240</td>
</tr>
<tr>
<td>600 °C CLC</td>
<td>90</td>
<td>360</td>
<td>1350</td>
<td>240</td>
</tr>
<tr>
<td>700 °C CLC</td>
<td>90</td>
<td>360</td>
<td>1350</td>
<td>240</td>
</tr>
<tr>
<td>800 °C CLC</td>
<td>90</td>
<td>360</td>
<td>1350</td>
<td>240</td>
</tr>
<tr>
<td>850 °C CLC</td>
<td>90</td>
<td>360</td>
<td>1350</td>
<td>240</td>
</tr>
<tr>
<td>900 °C CLC</td>
<td>90</td>
<td>360</td>
<td>1350</td>
<td>240</td>
</tr>
<tr>
<td>950 °C CLC</td>
<td>90</td>
<td>360</td>
<td>1350</td>
<td>240</td>
</tr>
<tr>
<td>1000 °C CLC</td>
<td>90</td>
<td>360</td>
<td>1350</td>
<td>240</td>
</tr>
<tr>
<td>GGBS</td>
<td>90</td>
<td>360</td>
<td>1350</td>
<td>240</td>
</tr>
<tr>
<td>PFA</td>
<td>90</td>
<td>360</td>
<td>1350</td>
<td>240</td>
</tr>
<tr>
<td>Silica fume</td>
<td>90</td>
<td>360</td>
<td>1350</td>
<td>240</td>
</tr>
<tr>
<td>Ground sand</td>
<td>90</td>
<td>360</td>
<td>1350</td>
<td>240</td>
</tr>
</tbody>
</table>

- CLC = calcined London clay

The mixing of CEM-I, silica sand, test materials and water was conducted in a planetary orbital mortar mixer (ELE international, UK). The pre-set mixing program was used at a low speed for 30 seconds, as soon as water and binder were mixed. Sand was steadily added during the next 30 seconds of low speed mixing, which was then followed by a high speed mixing lasting for 30 seconds. After a short pause of 90 seconds for mixing quality control, the whole process finished with a one-minute mixing at the high speed. Fresh mortar was cast into steel moulds on a vibration table to form cubes with an identical dimension of 50x50x50 mm. All cubes were demoulded 24 hours later, and kept in a water bath at 23 °C until different selected test times. On the 3, 7, 14, 28, 90 and 180-day, cubes were removed from the water bath, surface dried and tested for compressive strengths using a concrete compression machine (Controls, UK) with a loading rate of 0.3 MPa/s. Since each mortar cube sample was made in triplicate, the reported compressive strengths are the averages of three parallel tests. SAI test results are presented in the form of percentage as follows:

\[ SAI = \frac{A}{B} \times 100\% \]
where $A$ is the compressive strength of the test mortar at the selected curing time (MPa) and $B$ is the compressive strength of the control mortar at the same curing age (MPa).

c) **Portlandite consumption test**

As mentioned previously, pozzolanic reaction takes place between SCMs and Ca(OH)$_2$ in the presence of free water to form C-S-H, C-A-H or C-A-S-H phases. Since it is complicated and difficult to directly measure the amount of SCM that has been consumed in the pozzolanic reaction, an alternative way being commonly adopted to study the progress of the reaction is to determine the consumption of Ca(OH)$_2$. Frattini test is a method that exactly applies to that route, and the following test performed with TGA is another. TGA was one of the analytical techniques used to characterize the as-received London clay, and it is capable of monitoring how the sample weight is affected by increasing temperature. It is widely understood that the decomposition of calcium hydroxide into water and calcium oxide happens approximately between 350 ~ 550 °C (El-Jazairi & Illston, 1977). For a sample containing unreacted Ca(OH)$_2$, the weight loss due to dehydration of Ca(OH)$_2$ within that particular temperature range can be measured by TGA. In this study, pastes for different materials were prepared and tested on TGA. The mix proportions of pastes are summarised in Table 4.3.

**Table 4.3** The mix proportions of pastes for portlandite consumption test

<table>
<thead>
<tr>
<th>Pastes</th>
<th>Test materials (g)</th>
<th>Ca(OH)$_2$ (g)</th>
<th>Water (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>600 °C CLC</td>
<td>10</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>700 °C CLC</td>
<td>10</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>800 °C CLC</td>
<td>10</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>850 °C CLC</td>
<td>10</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>900 °C CLC</td>
<td>10</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>950 °C CLC</td>
<td>10</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>1000 °C CLC</td>
<td>10</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>GGBS</td>
<td>10</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>PFA</td>
<td>10</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>Silica fume</td>
<td>10</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>Ground sand</td>
<td>10</td>
<td>10</td>
<td>20</td>
</tr>
</tbody>
</table>

- CLC = calcined London clay
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For each paste, analytical grade Ca(OH)$_2$ and a test material were mixed in the dry state in a glass beaker by hand for 1 minute. As soon as distilled water was added, the whole mixture was stirred for 2 more minutes. Subsequently, the paste was poured into a plastic cylinder container for curing. The container was sealed with cling film and capped, and then stored in an oven at 40 °C. A fraction of sample was taken out from the paste and then placed in a freeze dryer for 48 hours to stop hydration on the 3-day. The rest of paste was sealed again and returned to the oven. After being removed from the freeze dryer, the sample was tested immediately in the TGA instrument or stored in a desiccator waiting for instrument availability. On the 7, 14, 28 and 90-day, the above procedures for sampling and testing were repeated for the same paste. All the TGA measurements were performed with a Polymer Laboratories Thermal Science STA 1500 analyser (Polymer Laboratories, USA) at a heating rate of 10 °C/min from 30 °C to 1000 °C in a nitrogen environment. This heating rate was different from that used in the characterization of as-received London clay, which was 15 °C/min. The change in heating rate was intended to further ensure the accuracy of the TGA measurements in the portlandite consumption test. The measurement for each test material was in triplicate, and therefore the reported result is the average of three.

In literatures, there has been no universally adopted method with regard to the interpretation of TGA curve for determining Ca(OH)$_2$ content. An improper interpretation may induce significant errors and consequently cause inaccurate results. In this study, a method suggested by Kim & Olek (2012) was used to interpret TGA curves, as shown in Figure 4.1.

The start point temperature and end point temperature for Ca(OH)$_2$ decomposition were selected using the second derivative curve. The mass loss due to the dehydration of Ca(OH)$_2$ was calculated from a vertical distance between two tangential lines. The vertical distance was taken at the inflection point of TGA curve, which can be identified on the first derivative curve without any difficulty. This interpretation is based on an assumption that the mass loss for the decomposition of other hydrates is continuous and takes place at the rate coinciding with the slope of the temperature between the start point and the end point (Kim & Olek, 2012). In this method, carbonation effect on samples was taken into account to ensure a more accurate final result. As can be seen in Figure 4.1, the mass loss due to the decomposition of CaCO$_3$
was obtained through the same way, but it is worth mentioning that the tangential line used for the determination of the start point of CaCO\textsubscript{3} decomposition was the same used to determine the end point of Ca(OH)\textsubscript{2} dehydration. This is because the decomposition of CaCO\textsubscript{3} occurs over a wider temperature range and the start point is not as clear as that of Ca(OH)\textsubscript{2} (Kim & Olek, 2012). In addition, carbonation may also happen to the original Ca(OH)\textsubscript{2} before that was used to prepare different pastes. Measurement and deduction for that kind of CaCO\textsubscript{3} formed in the original Ca(OH)\textsubscript{2} was performed accordingly.

![Figure 4.1 Interpretation of TGA curves (Kim & Olek, 2012) (deriv. = derivative)](image)

**Figure 4.1** Interpretation of TGA curves (Kim & Olek, 2012) (deriv. = derivative)

**d) Chapelle test**

Chapelle test was used in this research, making the assessment of pozzolanic reactivity for SCMs more comprehensive. It is similar to Frattini test in respect of principles behind and operations needed. Specifically, it allows SCMs to react with
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Ca(OH)$_2$ in an abundance of water and also involves chemical titration to determine the concentration of Ca(OH)$_2$ in the filtrate. For the differences, heating samples to a higher temperature of around 85 °C is adopted in Chapelle test, while samples in Frattini test are kept at 40 °C prior to vacuum filtration and titration. Moreover, samples are allowed to cure for 8 and 15 days in Frattini test, whereas samples in Chapelle test are usually vacuum filtered and analysed by titration immediately after 16 hours.

The procedures of Chapelle test were slightly adapted from literatures (Quarcioni et al, 2015; Ferraz et al, 2015). As-received clay, calcined clays, GGBS, PFA, silica fume and ground silica sand were all tested. 1 g of test material, 2 g of CaO and 250 ml of distilled water were delivered to a dry clean Erlenmeyer flask. A magnetic stirrer hotplate was employed to heat up the content within the Erlenmeyer flask to a temperature of 85 ± 5 °C and stir that with the aid of a magnetic stir bar simultaneously. A thermometer was used to verify the temperature had reached the required range, and the evaporation of water was prevented using a condenser. The heating and stirring was kept for 16 hours. A schematic illustration for this part of process is shown in Figure 4.2. The heating was stopped after 16 hours, allowing the mix to cool to ambient temperature. Subsequently, 250 ml of sucrose solution freshly made by dissolving 60 g of sucrose was added into the Erlenmeyer flask, and the stirring was allowed to keep running for 15 more minutes. After the mix was vacuum filtered using a filter paper with a nominal pore size of 2.7 µm (Whatman 542), the filtrate was analysed for the concentration of OH$^-$ by conducting titration against 0.1 mol/l hydrochloric acid with phenolphthalein used as the indicator. A blank sample containing only CaO and distilled water was prepared and tested following the same procedures. The reported results of Chapelle test are expressed in mg of Ca(OH)$_2$ fixed by per gram of test material as follows:

$$
result = 2 \times \frac{V1 - V2}{V1} \times \frac{74}{56} \times 1000
$$

where result refers to mg of Ca(OH)$_2$ fixed by per gram of test material, $V1$ (ml) refers to the volume of HCl used in the blank sample measurement, and $V2$ (ml) refers to the volume of HCl used in the test material measurement.

The measurement for each test material was in triplicate, and therefore the reported result is the average of three.
Figure 4.2 Assembly of the Chepelle test equipments
4.2.5 Preparation of concrete samples

a) Preparation of calcined London clay for making concrete

Dried ground as-received London clay always presented a reddish and brownish colour after calcining, which is due to the oxidation reaction of iron-containing minerals in the clay. In order to diminish the colour distinction between calcined London clay and ordinary Portland cement and make the concrete containing calcined clay visually resembling the conventional, a special calcining method was developed to process as-received London clay for concrete samples testing. In addition, the details about the cause of colour change will be discussed in Chapter 7.

The raw clay was kneaded into spherical lumps with a diameter of around 5 cm, and the lumps were stored in an oven at 110 °C for at least 24 hours to remove moisture. The dried lumps were afterwards calcined in a chamber furnace (Carbolite, UK) at the 900 °C for 2 hours. The calcined clay was then ground into a fine powder using a vibratory disc mill (Gy-Ro, Glen Creston Ltd, UK) for 2 minutes. The median particle size and the specific gravity were determined to be 10.4 µm and 2.88, respectively. Figure 4.3 shows the appearances of lumps before and after calcining, the internal area of a calcined lump, and the calcined clay powder resulting from grinding calcined lumps.
Figure 4.3 (a) Moist clay made into spherical lumps was ready to be oven-dried. (b) Calcined London clay lumps. The surface appeared to be orange. The presence of crack was due to loss of moisture in oven. (c) Calcined clay was hammered to show black core. (d) Ground calcined London clay.

It is worth mentioning that the calcining of dried clay lumps was attempted to run in the way that a second batch was put into the furnace as soon as the first batch finished and was removed for cooling. However, due to the sudden rise of ambient temperature, the air trapped in the second batch of dried clay lumps expanded rapidly and caused the lumps to burst. Therefore, allowing the interior temperature of furnace to cool to around 110 °C before starting next batch is indispensable.

b) Concrete mix design

The concrete mix proportion calculation was based on the “absolute volume method” (Neville, 1996). The method assumes that the volume of a fully compacted concrete is equal to the sum of the absolute volumes of all components. The calculation is explained on 1 m$^3$ concrete basis for convenience.

\[
\frac{m_w}{\rho_w} + \frac{m_c}{\rho_c} + \frac{m_{A_1}}{\rho_{A_1}} + \frac{m_{A_2}}{\rho_{A_2}} + \frac{m_A}{\rho_A} = 1
\]

$W = \text{water}, C = \text{cement}, A_1 = \text{fine aggregate}, A_2 = \text{coarse aggregate}, A = \text{Air}$

$m_x = \text{mass of } x, \rho_x = \text{density of } x$
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It is assumed in this method that all solid state components are completely dry and the entrapped air accounts for 1% of the total volume. It is also designed that 65% of the total concrete volume is occupied by coarse and fine aggregates. If the densities of all components are known, the mass of each component can be worked out for a given water-to-binder ratio. When the w/b ratio is 0.5,

$$\frac{m_w}{\rho_w} + \frac{m_c}{\rho_c} + \frac{m_{A1}}{\rho_{A1}} + \frac{m_{A2}}{\rho_{A2}} + \frac{m_A}{\rho_A} = 1$$

Since \( \frac{m_w}{m_c} = 0.5, \frac{m_{A1}}{m_c} = 0.65, \frac{m_{A2}}{m_c} = 0.01 \)

$$\frac{0.5m_c}{\rho_w} + \frac{m_c}{\rho_c} + 0.65 + 0.01 = 1$$

$$\frac{0.5m_c}{1000} + \frac{m_c}{3150} + 0.65 + 0.01 = 1$$

\( m_c = 416\text{kg} \)

\( m_w = 416 \times 0.5 = 208\text{kg} \)

If the mass ratio of fine aggregate to all aggregate is designed to be 0.35, the calculation continues as follows.

$$\frac{208}{1000} + \frac{416}{3150} + \frac{7}{13} \frac{m_{A2}}{2580} + \frac{m_{A2}}{2420} + 0.01 = 1$$

\( m_{A2} = 1045\text{kg} \)

\( m_{A1} = 1045 \times \frac{7}{13} = 563\text{kg} \)

The values of \( m_w, m_c, m_{A1}, m_{A2} \) and \( m_A \) have all been worked out.

When a SCM is incorporated into the concrete mix as a cement replacement, the mass of each component has to be altered accordingly. For a concrete mix containing a SCM to substitute 20 wt.% of cement, the mass of SCM can be calculated as follows (the adjusted masses in blended mix are denoted by ‘).

\( m_c' = m_c \times 0.8 = 333\text{kg} \)

\( m_{\text{SCM}'} = m_c \times 0.2 = 83\text{kg} \)
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Neville (1996) suggested that when an extra term is introduced into the absolute volume equation, the mass of coarse aggregate should be maintained and the adjustment should be made to the mass of fine aggregate. A replacement of 20 wt.% is still taken as an example here.

\[
\frac{m_w}{\rho_w} + \frac{m_c}{\rho_c} + \frac{m_{A1}'}{\rho_{A1}} + \frac{m_{A2}}{\rho_{A2}} + \frac{m_A}{\rho_A} + \frac{m_{SCM}'}{\rho_{SCM}} = 1
\]

\[
\frac{208}{1000} + \frac{333}{3150} + \frac{m_{A1}'}{2580} + \frac{1045}{2420} + 0.01 + \frac{83}{2880} = 1
\]

\[m_{A1}' = 557\text{kg}\]

In this study, three different w/b ratios (0.3, 0.4 and 0.5) were used to prepare concrete samples containing calcined London clay. At each w/b ratio, a range of levels (0, 10, 20 and 30 wt.%) were adopted to replace CEM-I with calcined London clay. PFA, GGBS and silica fume were used at a common w/b ratio of 0.4 and a common substitution level of 20 wt.% to manufacture concrete samples. The complete mix proportions of concrete samples are given in Table 4.4.
### Table 4.4 The mix proportions of concrete

<table>
<thead>
<tr>
<th>Mix</th>
<th>w/b ratio</th>
<th>Water (kg/m³)</th>
<th>CEM I (kg/m³)</th>
<th>SCM (%)</th>
<th>SCM (kg/m³)</th>
<th>Fine aggregate (kg/m³)</th>
<th>Coarse aggregate (kg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Series I</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-0.5-000</td>
<td>0.5</td>
<td>208.0</td>
<td>415.9</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>562.8</td>
</tr>
<tr>
<td>C-0.5-10C</td>
<td>0.5</td>
<td>208.0</td>
<td>374.3</td>
<td>10</td>
<td>41.6</td>
<td>-</td>
<td>559.8</td>
</tr>
<tr>
<td>C-0.5-20C</td>
<td>0.5</td>
<td>208.0</td>
<td>332.7</td>
<td>20</td>
<td>83.2</td>
<td>-</td>
<td>556.9</td>
</tr>
<tr>
<td>C-0.5-30C</td>
<td>0.5</td>
<td>208.0</td>
<td>291.2</td>
<td>30</td>
<td>124.8</td>
<td>-</td>
<td>554.0</td>
</tr>
<tr>
<td>C-0.4-000</td>
<td>0.4</td>
<td>189.6</td>
<td>473.9</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>562.8</td>
</tr>
<tr>
<td>C-0.4-10C</td>
<td>0.4</td>
<td>189.6</td>
<td>426.5</td>
<td>10</td>
<td>47.4</td>
<td>-</td>
<td>559.4</td>
</tr>
<tr>
<td>C-0.4-20C</td>
<td>0.4</td>
<td>189.6</td>
<td>379.1</td>
<td>20</td>
<td>94.8</td>
<td>-</td>
<td>556.1</td>
</tr>
<tr>
<td>C-0.4-30C</td>
<td>0.4</td>
<td>189.6</td>
<td>331.7</td>
<td>30</td>
<td>142.2</td>
<td>-</td>
<td>552.7</td>
</tr>
<tr>
<td>C-0.3-000</td>
<td>0.3</td>
<td>165.2</td>
<td>550.6</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>562.8</td>
</tr>
<tr>
<td>C-0.3-10C</td>
<td>0.3</td>
<td>165.2</td>
<td>495.6</td>
<td>10</td>
<td>55.1</td>
<td>-</td>
<td>558.9</td>
</tr>
<tr>
<td>C-0.3-20C</td>
<td>0.3</td>
<td>165.2</td>
<td>440.5</td>
<td>20</td>
<td>110.1</td>
<td>-</td>
<td>555.0</td>
</tr>
<tr>
<td>C-0.3-30C</td>
<td>0.3</td>
<td>165.2</td>
<td>385.5</td>
<td>30</td>
<td>165.2</td>
<td>-</td>
<td>551.1</td>
</tr>
<tr>
<td><strong>Series II</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-0.4-20P</td>
<td>0.4</td>
<td>189.6</td>
<td>379.1</td>
<td>20</td>
<td>-</td>
<td>94.8</td>
<td>539.8</td>
</tr>
<tr>
<td>C-0.4-20S</td>
<td>0.4</td>
<td>189.6</td>
<td>379.1</td>
<td>20</td>
<td>-</td>
<td>94.8</td>
<td>537.7</td>
</tr>
<tr>
<td>C-0.4-20G</td>
<td>0.4</td>
<td>189.6</td>
<td>379.1</td>
<td>20</td>
<td>-</td>
<td>94.8</td>
<td>560.5</td>
</tr>
</tbody>
</table>

* CLC = Calcined London Clay (900°C), * SF = Silica Fume
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For each concrete mix in this study, a total of 15 cubes (100x100x100 mm) were required, which made the theoretical volume of each fresh concrete be 15 L. For allowing the inevitable loss during the mixing and transferring process, 17 L of fresh concrete was prepared for each mix.

The natural moisture and absorption of the used aggregates were measured to be 0.49% and 3.06% for coarse aggregate, and 0.44% and 0.63% for fine aggregate, respectively. Based on these results, an adjustment was made to the amounts of water, coarse and fine aggregates required to produce 17 L of fresh concrete.

c) Preparation of fresh concrete

A 40-L pan and paddle driven mixer (Zyklos, Pemat, Germany) was employed to mix raw materials. At the start, a wet towel was used to wipe the inside surface of the mixer, followed by a second wiping using a dry towel. This ensured it was surface-dry, preventing it from detaining water from concrete mix. Raw materials were accurately weighed to the adjusted amounts for producing 17 L of fresh concrete. The coarse and fine aggregates and half of the water were added first for a 3-minute mixing. For those mixes containing SCMs, CEM-I was mixed with SCMs in the dry state by hand before they were added into the mixer. Following that, the binder (CEM-I or CEM-I plus SCMs) and the other half of the water were added for another 3 minutes of mixing.
4.2.6 Tests for concrete samples

a) Slump test for fresh concrete

The slump test was performed for each concrete mix. A metal mould of frustum shape was filled up with fresh concrete in three layers. Each layer was tamped using a metal rod for 25 times before filling up next layer. When the mould was full, it was lifted up vertically, allowing the freed fresh concrete to slump. The rod was then placed on the top of the mould, assisting the measurement of the distance between it and the highest point of collapsed fresh concrete. The whole slump test procedures were repeated so that an average result can be obtained and recorded. The apparatuses and schematic illustration of slump test for fresh concrete is shown in Figure 4.4.

![Figure 4.4](image)

Figure 4.4 (a) Set-up of a slump test: Metal mould, compacting rod and a non-absorbent surface. (b) Schematic illustration of slump measurement

b) Casting of concrete cubes

After the slump test, the concrete was immediately returned the mixer for a quick remixing for 1 minute. It was then cast into plastic moulds (Controls, UK) in a dimension of 100x100x100 mm. In order to achieve a good compaction, the casting was carried out in a three-layer way on a vibration table. When the moulds were full with concrete, the vibration was not stopped until there were no visible air bubbles emerging on the top surface of concrete. Polystyrene boards were used to cover the top of the filled moulds upon the completion of casting. This helped prevent the evaporation of free water which could impact the actual w/b ratio of concrete and moreover enabled the moulds to provide an insulation environment to concrete within them. It was understood that the loss of hydration heat could induce inconsistency to hydration reaction at early age and therefore cause adverse impact to strength development (Durán-Herrera et al, 2007). All cube samples were allowed to stay in the moulds
covered by the polystyrene boards for 24 hours. They were demoulded next day by using compressed air.

**c) Water bath curing**

As a concrete sample can reach up to 60 °C during hydration under an insulation condition, a sudden exposure to room temperature (demoulding) may cause significant micro-cracking to the surface of concrete by thermal shock. Durán-Herrera et al (2007) suggested that curing the sample in water for some days would be able to heal the cracks.

In this study, curing in water bath was preferred rather than in air with 100% relative humidity. This is because Hewlett (2003) reported that curing in humid air was slow and incomplete. Siddique (2014) suggested that concrete could gain higher strength by water curing than by humid air curing within a same period. Figure 4.5 shows the mixer and the mould employed in this study.

![Figure 4.5](image) (a) 40-L mixer used to blend raw materials and prepare concrete mix. (b) Plastic mould used for casting

**d) Density measurement**

The densities of concrete cubes were measured employing a specific gravity balance (Stable Micro Systems, UK), which was shown in Figure 4.6. For each measurement,
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A cube was first placed onto the sample suspender, and fully immersed into water. When the reading on the balance became stable, the weight was recorded. The cube was then removed from water, and surface-dried by using wet cloth. It was lastly placed on the silver plate for measuring the weigh in air. According to Archimedes’ Principle, the density of the cube can be worked out from the above two measurements, given that the density of water was 1000 kg/m$^3$. Cubes were triplicate for each concrete mix on each testing day, and therefore an average of three was drawn.

The process of calculation is given as follows.

\[ g = \text{acceleration due to gravity}, \quad \rho_x = \text{density of } x, \quad m_x = \text{mass of } x \]

\[ V = \text{volume of concrete} \]

Force exerted by scale = Weight of concrete in water = Weight of water displaced

Buoyance force = $\rho_{\text{water}}gV$

Force balance: \[ m_{\text{concrete}}g = m_{\text{water}}g + \rho_{\text{water}}gV \]

\[ V = \frac{m_{\text{concrete}} - m_{\text{water}}}{\rho_{\text{water}}} \]

\[ \rho_{\text{concrete}} = \frac{m_{\text{concrete}}}{V} = \frac{m_{\text{concrete}}}{m_{\text{concrete}} - m_{\text{water}}} \times \rho_{\text{water}} \]

\[ \text{Figure 4.6 (a) Specific gravity balance used to measure concrete density. (b) Schematic diagram of set-up to show force balance} \]
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e) Compressive strength tests

After each concrete mix was cast, compressive strength testing was carried out on a compression machine (Controls 3000kN load cell, UK) on the 3rd, 7th, 14th, 28th and 90th days. The loading rate was set to 0.3 MPa/s, in compliance with ASTM C39. For each concrete mix on each testing day, cubes were triplicate so that an average of three can be obtained.
Chapter 5 CHARACTERIZATION
5.1 X-ray fluorescence (XRF) analysis

The chemical compositions of as-received London clay were determined by conducting XRF analysis. The CEM-I, PFA, GGBS and silica fume used in this study were also examined in terms of chemical compositions, and all the results are reported in Table 5.1.

Table 5.1 Chemical compositions of studied materials

<table>
<thead>
<tr>
<th>Oxides</th>
<th>As-received London clay (%)</th>
<th>CEM-I (%)</th>
<th>PFA (%)</th>
<th>GGBS (%)</th>
<th>Silica fume (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>45.8</td>
<td>21.0</td>
<td>54.8</td>
<td>31.8</td>
<td>94.0</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>12.8</td>
<td>4.4</td>
<td>21.3</td>
<td>10.8</td>
<td>-</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>7.7</td>
<td>2.7</td>
<td>12.1</td>
<td>0.3</td>
<td>1.0</td>
</tr>
<tr>
<td>K₂O</td>
<td>3.7</td>
<td>1.4</td>
<td>3.0</td>
<td>1.0</td>
<td>1.6</td>
</tr>
<tr>
<td>MgO</td>
<td>1.8</td>
<td>1.6</td>
<td>-</td>
<td>17.2</td>
<td>2.5</td>
</tr>
<tr>
<td>CaO</td>
<td>1.1</td>
<td>64.7</td>
<td>4.3</td>
<td>35.4</td>
<td>0.2</td>
</tr>
<tr>
<td>TiO₂</td>
<td>1.3</td>
<td>-</td>
<td>1.1</td>
<td>0.4</td>
<td>-</td>
</tr>
<tr>
<td>SO₃</td>
<td>1.3</td>
<td>3.1</td>
<td>2.1</td>
<td>2.7</td>
<td>0.7</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.9</td>
<td>0.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

The investigation of the origin of each element found in the as-received London clay sample was carried out on the basis of XRD analysis results. The high SiO₂ and Al₂O₃ content is particularly typical for clay, due to the presence of quartz, feldspar and various clay minerals. Iron is found to be the third most abundant element in the London clay. It may derive from not only iron minerals, such as pyrite and goethite, but clay minerals, such as montmorillonite, illite and chlorite, where iron can serve as one of octahedral layer cations. It could also be present in kaolinite and montmorillonite as a lattice substitution for Si and Al atoms. Due to the high iron content, the as-received clay gains a reddish/brownish color after calcining at the studied temperatures. The color change originates from the formed hematite upon calcining. Details about the color change will be discussed later. The 3.7 wt.% K₂O is derived from illite and K-feldspar without any doubt. MgO is determined to account for 1.8 wt.% of as-received London clay. Its origin can be explained from two aspects, one of which is the role of
Chapter 5 Characterization

octahedral layer cation in illite, montmorillonite and chlorite. The other is associated with the brucite layer within the structure of chlorite.

Figure 5.1 shows a ternary phase diagram of SiO$_2$, Al$_2$O$_3$ and CaO. All the studied materials are located within the diagram, according to their normalized compositions of SiO$_2$, Al$_2$O$_3$ and CaO. The typical areas of Portland cement, slag, PFA, natural pozzolans and silica fume are patterned and labelled on the figure, according to the work made by Lothenbach, Scrivener & Hooton (2011).

![Figure 5.1](image.png)

Figure 5.1 The typical areas of Portland cement, slag, PFA, natural pozzolans and silica fume within a ternary phase diagram of SiO$_2$, Al$_2$O$_3$ and CaO (Lothenbach, Scrivener & Hooton, 2011), and the locations of studied materials

It is manifest that the studied materials are all located within the reported typical areas on Figure 5.1. Particularly, the as-received London clay is located within the area of natural pozzolans, which has a considerably large overlapping with the PFA area. As is well understood, Portland cement is a hydraulic material and GGBS is a latent hydraulic material. Their locations together with those of silica fume, PFA and natural pozzolans on the ternary phase diagram indicates a trend that the higher the CaO content, the higher the hydraulic reactivity.
5.2 Density measurement

Density measurement was performed for the materials, and the results are reported in the Table 5.2. For calcined London clays, the densities were measured after the previously mentioned re-grinding.

Table 5.2 Results of density measurement

<table>
<thead>
<tr>
<th>Materials</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-received clay</td>
<td>2.6</td>
</tr>
<tr>
<td>600 °C CLC</td>
<td>2.8</td>
</tr>
<tr>
<td>700 °C CLC</td>
<td>2.8</td>
</tr>
<tr>
<td>800 °C CLC</td>
<td>2.8</td>
</tr>
<tr>
<td>850 °C CLC</td>
<td>2.7</td>
</tr>
<tr>
<td>900 °C CLC</td>
<td>2.9</td>
</tr>
<tr>
<td>950 °C CLC</td>
<td>2.7</td>
</tr>
<tr>
<td>1000 °C CLC</td>
<td>2.7</td>
</tr>
<tr>
<td>PFA</td>
<td>2.4</td>
</tr>
<tr>
<td>GGBS</td>
<td>3.1</td>
</tr>
<tr>
<td>Silica fume</td>
<td>2.4</td>
</tr>
<tr>
<td>Ground sand</td>
<td>2.7</td>
</tr>
</tbody>
</table>

- CLC = calcined London clay

As a result of calcining and re-grinding, density of calcined London clay is found to be slightly increased, compared with that of as-received clay. This can be attributed to the loss of structural water on calcining. However, there seems to be no correlation between calcining temperature and density. The densities of calcined clays vary in the range of 2.7–2.9 g/cm³. PFA and silica fume exhibit the lowest density of 2.4 g/cm³ while GGBS shows the highest (3.1 g/cm³) amongst all.
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5.3 Particle size analysis by laser diffraction

Based on the current knowledge of the mechanisms of filler effect and pozzolanic reaction, particle size is an extremely critical parameter in the studies of cement replacement materials. In this work, the measurement of particle size for as-received clay, calcined clays, PFA, GGBS, silica fume and sand was carried out by employing laser diffraction technique.

As described in Section 4.2.1, the excavated London clay was ground, in a dry state, for 1 minute to produce the 'as-received' clay that was ready for calcining at different temperatures. During the calcining process, the agglomeration of clay particles would occur, due to sintering phenomenon. It was depicted in Section 4.2.2 that all the calcined clay samples were re-ground in the same mill for 2 minutes, in order to diminish the effect of particle agglomeration and ensure a relatively consistent particle fineness for all the calcined clay samples. The particle size distribution of calcined clay samples before and after re-grinding is illustrated in Figure 5.2.

![Figure 5.2 Particle size distribution of calcined clay before and after re-grinding](image-url)
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It is manifest in Figure 5.2 that, due to the occurrence of particle agglomeration, the particle fineness without re-grinding decreases as the calcining temperature rises. The re-grinding can effectively improve the particle fineness of calcined products.

Figure 5.3 shows the particle size distribution of all the re-ground calcined clay samples as well as PFA, GGBS, silica fume, ground sand and as-received clay. In addition, the $d_{10}$, $d_{50}$ and $d_{90}$ values for all the materials are presented in Table 5.3. The value of the particle diameter at 10% in the cumulative distribution is referred to as $d_{10}$, and similar definitions apply to $d_{50}$ and $d_{90}$.

Figure 5.3 Particle size distribution of the re-ground calcined clay and other test materials
Table 5.3 \( d_{10}, d_{50} \) and \( d_{90} \) values for all the materials

<table>
<thead>
<tr>
<th>Materials</th>
<th>( d_{10} ) (µm)</th>
<th>( d_{50} ) (µm)</th>
<th>( d_{90} ) (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-received clay</td>
<td>1.8</td>
<td>9.0</td>
<td>50.8</td>
</tr>
<tr>
<td>600 °C CLC</td>
<td>1.1</td>
<td>8.2</td>
<td>34.5</td>
</tr>
<tr>
<td>700 °C CLC</td>
<td>1.2</td>
<td>11.5</td>
<td>58.4</td>
</tr>
<tr>
<td>800 °C CLC</td>
<td>1.1</td>
<td>10.4</td>
<td>58.2</td>
</tr>
<tr>
<td>850 °C CLC</td>
<td>1.0</td>
<td>8.5</td>
<td>58.9</td>
</tr>
<tr>
<td>900 °C CLC</td>
<td>0.9</td>
<td>7.0</td>
<td>48.0</td>
</tr>
<tr>
<td>950 °C CLC</td>
<td>0.9</td>
<td>4.6</td>
<td>31.7</td>
</tr>
<tr>
<td>1000 °C CLC</td>
<td>0.9</td>
<td>5.1</td>
<td>35.7</td>
</tr>
<tr>
<td>PFA</td>
<td>1.9</td>
<td>15.3</td>
<td>72.1</td>
</tr>
<tr>
<td>GGBS</td>
<td>1.6</td>
<td>16.1</td>
<td>81.3</td>
</tr>
<tr>
<td>Silica fume</td>
<td>0.9</td>
<td>6.9</td>
<td>18.8</td>
</tr>
<tr>
<td>Ground sand</td>
<td>1.5</td>
<td>21.6</td>
<td>161.5</td>
</tr>
</tbody>
</table>

- CLC = calcined London clay

As can be seen from Figure 5.3 and Table 5.3, after the re-grinding, all the calcined clay samples show similar particle size distributions with a \( d_{10} \) of around 1 µm, a \( d_{50} \) of around 10 µm and a \( d_{90} \) of less than 60 µm. PFA and GGBS have a slightly lower particle fineness than calcined clays while silica fume possesses the highest amongst all the tested materials. Ground sand is coarser than any other material in this study.

These particle size distribution data given by laser diffraction analysis are only estimates of the true particle fineness. This is due to the irregular shape of clay particles and the difficulty of laser diffraction technique in defining the size of irregularly shaped particles (Eshel et al, 2004).
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5.4 Scanning electron microscopy (SEM)

The particle morphology of as-received clay, re-ground calcined clays, PFA, GGBS and silica fume was carefully examined under SEM at the secondary electrons mode. The corresponding images are given in the following Figure 5.4, 5.5, 5.6, 5.7 and 5.8, respectively.

![Image of as-received London clay under SEM](image1)

**Figure 5.4** The particle morphology of as-received London clay (x800)

![Image of 900 °C calcined London clay under SEM](image2)

**Figure 5.5** The particle morphology of 900 °C calcined London clay (x1500)
Figure 5.6 The particle morphology of PFA (×1500)

Figure 5.7 The particle morphology of GGBS (×1500)
Figure 5.8 The particle morphology of densified silica fume: a) ×300 magnification, b) ×1500 magnification

As-received clay particles that are ready for calcining exhibit an irregular shape in the SEM image. Similar irregular-shaped particles are observed for 900 °C calcined clay in Figure 5.5. There is no noticeable change on the particle morphology under SEM secondary electrons mode after calcining at 900 °C for 2 hours. In addition, no
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difference was found between different calcining temperatures in terms of the morphology of calcined products. 900 °C calcined clay is therefore selected as an example to be compared with as-received clay. The morphology of the London clay samples calcined at 600, 700, 800, 850, 950 and 1000 °C can be found in the Appendix.

As shown in Figure 5.6 and 5.7, PFA particles have a well-known spherical shape while GGBS particles are mostly flaky in the image. Figure 5.8 a) and b) show the morphology of densified silica fume at different magnifications.
5.5 X-ray diffraction (XRD)

As-received and calcined London clay samples were all examined on an X-ray diffractometer for understanding the impact of calcining temperatures on the crystallinity of clay and non-clay minerals. As the samples under investigation were prepared to stay randomly oriented, all the reflections, including $00l$ and $hkl$, were expected to be observable on the diffractograms. However, some peaks are inevitably masked by others, which makes the mineral identification work more difficult and complicated. This is because London clay is in fact a complex mixture of various clay and non-clay minerals. One possible solution to confirm the existence of a particular clay mineral from an overlapped peak could be looking at the diffractogram corresponding to a higher calcining temperature that can cause decomposition of the particular mineral but induce no impact on the crystallinity of the other mineral. A good example is the identification between kaolinite and illite in the lower $2\theta$ angle range, and the relevant details are given later. The XRD data (diffractograms) for a full range $2\theta$ angle from 5°$2\theta$ to 70°$2\theta$ is shown in Figure 5.9.
Figure 5.9 XRD patterns of as-received and calcined clay samples
Chapter 5 Characterization

As can be seen in Figure 5.9, a number of distinctive peaks survived from being calcined at up to 1000 °C for 2 hours. They are recognised as reflections from quartz and feldspar, which are the second most and the most abundant minerals in the earth’s crust (Wenk & Bulakh, 2004) and both considered to be inert in terms of pozzolanic reaction. It is well known that quartz (SiO$_2$) is a tectosilicate mineral (or framework silicate) which can exist in two structural forms, α-quartz (or low quartz) and β-quartz (or high quartz). α-quartz is stable under the atmospheric pressure within a relatively broad temperature range, but it can be transformed to β-quartz when the temperature is above 573 °C, which is the so-called quartz inversion (Deer, Howie & Zussman, 1992). However, the inversion process is reversible upon cooling down. In this study, since all the calcining temperatures were higher than 573 °C, it is believed that α-quartz was ever transformed into β-quartz by calcining but the inversion took place in the reverse way during cooling. All the quartz peaks have been confirmed by ICDD reference database that they correspond to α-quartz. According to Figure 5.9, calcining treatment did not result in any apparent crystallinity reduction for feldspars, which are also a group of tectosilicate minerals. ICDD reference database indicates that all the relevant peaks are attributed to the reflections from K-feldspar (potassium feldspar), and this is in a good agreement with the XRF analysis results, which shows that K$_2$O accounts for 3.7 wt.% of as-received London clay. It is worth mentioning that, depending on surrounding temperature and pressure, K-feldspar can be present in two distinctive structural forms, which are orthoclase and microcline (KAlSi$_3$O$_8$). It is understood that microcline is the polymorph that is stable at lower temperatures (Dixon, Weed & Dinauer, 1977). This suggests the K-feldspar polymorph present in all the samples should be microcline. XRD measurements were carried out after all calcined samples cooled down to room temperature, which could further explain the presence of microcline in calcined clays. In addition, it should also be noted that apart from K-feldspar the peak at 13.7 °2θ could possibly be attributed to albite (NaAlSi$_3$O$_8$), which is a sodium-containing feldspar. This could be an explanation for the Na$_2$O constituent in the as-received London clay as shown by XRF results.

Since the majority of important peaks are not distinctive enough at a scale like Figure 5.9, the whole diffractogram is therefore divided into three parts, covering the same 2θ range from 5 to 70 °2θ, as shown in Figure 5.10.
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a) from 5 to 15 °2θ (c: chlorite, i: illite, k: kaolinite, m: montmorillonite)

b) from 15 to 40 °2θ (f: K-feldspar, g: goethite, h: hematite, p: pyrite, s: spinel)
c) from 40 to 70 °2θ (s: spinel)

**Figure 5.10** Diffractogram for as-received and calcined clay samples: a) from 5 to 15 °2θ, b) from 15 to 40 °2θ, c) from 40 to 70 °2θ

Chlorite, chemical formula \((\text{Si}_3\text{Al})\text{O}_{10}(\text{Mg}_3)(\text{OH})_2(\text{Mg}_2\text{Al})(\text{OH})\), was detected in the as-received London clay. It is known for chlorite that the brucite-like octahedral sheet incorporates approximately 75% of the whole structural water whilst the rest 25% is contained in the mica-like octahedral sheet (Piga, Villieras & Yvon, 1992). The dehydroxylation of the brucite-like layer takes place upon heating up to around 600 °C, which causes the (001) reflection a shift from about 6.3 to 6.4 °2θ and also an increase in intensity (Moore & Reynolds, 1997), as shown in Figure 5.10 a). Furthermore, the (002) reflection at 12.4 °2θ that overlaps with the (001) reflection of kaolinite disappears after the clay sample was calcined at 600 °C. At 700 °C, the (001) peak can still be recognized in the XRD spectra, but it disappears completely at 800 °C. This is because the mica-like layer of chlorite is dehydroxylated at this temperature. There is no remaining chlorite peak visible on the diffractogram when the calcining temperature is above 800 °C in this study.
Kaolinite reflections (001), (002), (-201), (1-31), (131), (133) and (060) are identified from the as-received London clay sample. As mentioned previously, kaolinite is a 1:1 clay mineral in terms of microstructure, combining one tetrahedral sheet with one octahedral sheet. This structure leaves the OH groups on the edge of the octahedral sheets directly exposed to the interlayer space, which facilitates the dehydroxylation of kaolinite. In the Figure 5.x a), b) and c), it can be clearly seen that all the kaolinite peaks disappear at 600 °C and higher temperatures. This indicates calcining at 600 °C can introduce a complete disorder to the crystal structure of kaolinite, and transform kaolinite into metakaolin. The result is in a good agreement with that of FTIR and TGA examinations.

According to XRD spectra, illite is present in the as-received London clay sample as well. The (004) and (-114) reflections are distinctive and do not overlap with any peaks corresponding to other minerals. Both of them are clearly visible in the as-received clay and when the calcining temperature is below 950 °C, which suggests illite can only be decomposed at 950 °C or higher. The (002) and (110) reflections overlap with the (001) and (110) reflections of montmorillonite, respectively. In addition, the (131) peak overlap with the (-201) reflection of kaolinite and the (104) reflection of montmorillonite. All these illite peaks are found to disappear when the calcining temperature reaches 950 °C. It is interesting to note that the peak at 35 °2θ that incorporates (131) of illite, (-201) of kaolinite and (104) of montmorillonite presents a relatively high shoulder before calcining. At 600 °C, the shoulder is weakened as well as the peak intensity, which can be attributed to the complete dehydroxylation of kaolinite. It seems to be very clear and simple that illite decomposes at 950 °C where no relevant peaks can be found on the XRD pattern. However, it was suggested that the dehydroxylation of illite in fact happens at about 550 °C but the crystal structure of illite is preserved and kept unchanged at the same temperature (Mackenzie, 1970; Fernandez, Martirena & Scrivener, 2011). In this study, the disappearance of all the illite peaks can only be observed at 950 °C and higher temperatures, which implies that 950 °C causes illite the complete loss of crystallinity. This is in accordance with the result from Fernandez (2009). For illite, dehydroxylation induces little impact on the crystallinity but the structured crystal can be destroyed at 950 °C and higher temperatures.
Montmorillonite is another important clay mineral found in the as-received London clay. As can be seen in Figure 5.x a), the reflection from the basal plane (001) overlaps with the (001) peak of chlorite at about 6.2 °2θ in the as-received clay sample. However, in the calcined samples, the (001) peak shifts to 8.9 °2θ where it overlaps with the (002) peak of illite. The shift is due to the removal of the water contained in the interlayer space. It is notable that, in the as-received clay sample, the overlapping between montmorillonite and chlorite at around 6.2 °2θ forms a small hump in the XRD pattern. That hump turns into a relatively sharp peak at almost the same 2θ angle for the 600 °C calcined clay sample. One reason for the change is, as discussed before, calcining at 600 °C makes the (001) reflection of chlorite slightly shift to the higher order with an increase in intensity. The other reason is that calcining leads to a complete dehydration of the interlayer space for montmorillonite and the (001) peak shifts from 6.2 to 8.9 °2θ. Due to this shift, the (002) reflection of illite appears more broad. All the montmorillonite peaks (overlapping with illite) are observable up to 900 °C. It is believed that the lattice structure of montmorillonite is destroyed completely at 950 °C. However, the reported dehydroxylation temperature range of the clay mineral is from 600 to 800 °C (Fernandez, Martirena & Scrivener, 2011). It is therefore the same case as for illite. Dehydroxylation does not make significant impact on the loss of crystallinity but the lattice structure is ruined at higher temperature. The thermal-driving amorphization process of illite and montmorillonite is apparently different from that of kaolinite. About the reason, Fernandez (2009) provided a possible explanation in his work that the amount of hydroxyls present in illite and montmorillonite is less than for kaolinite. He also concluded that the dehydroxylation of illite and montmorillonite is more likely to introduce a reorganization to the lattice structure rather than a proper disordering whilst, for kaolinite, the dehydroxylation leads to a complete loss of crystallinity.

In Figure 5.10 b) and c), at 950 °C two peaks appear at 37.1 °2θ and 65.4 °2θ, respectively. The former one is not clearly visible due to an overlapping with the quartz peak but the raised right shoulder of the quartz peak can indicate its presence. According to ICDD reference database, both peaks correspond to spinel (MgAl₂O₄), which is formed through the recrystallization in the calcining at 950 and 1000 °C. ICP test results (Table 5.5) support the idea because the concentration of Mg declines significantly at 850 °C when compared with 800 °C. This might imply the beginning of
recrystallization of spinel although the relevant reflections on the diffractogram are only observable at 950 and 1000 °C. It is manifest that recrystallization opposes the purpose of calcining, which is to transform as much as possible the crystalline phase into amorphous phase. The occurrence of recrystallization may explain the decrease in pozzolanic reactivity for 950 °C and 1000 °C calcined clay. Detailed discussion is given in the following chapter.

As suggested in Table 5.1, iron oxides constitute about 7.7 wt.% of as-received London clay. Although some of the iron could originate from the substitution for aluminium in the octahedral sheets of montmorillonite and illite, there are also some other iron-bearing minerals detected by XRD, such as pyrite (FeS$_2$), goethite (FeO(OH)) and hematite (Fe$_2$O$_3$). Pyrite can be decomposed at 400 °C (Hu et al, 2006), and therefore the peak at 37.1 °2θ is absent in all the calcined clay samples in this study. Goethite is only present (33.1 °2θ) in the as-received clay while the hematite reflections at 24.2, 33.3 and 35.7 °2θ appear in the calcined clay samples only. It is known that goethite can be transformed into hematite when temperature is above 300 °C (Hajpál & Török, 2004). This is exactly the case for goethite and hematite in this study.

Although the complete amorphization for all the clay minerals identified in the as-received London clay (chlorite, kaolinite, illite and montmorillonite) can be achieved only when the temperature is 950 °C or above, recrystallization of spinel seems to happen at 950 °C as well. As is well known and previously mentioned, recrystallization would have adverse effects on the pozzolanic reactivity of the material as a whole. 900 °C and 950 °C therefore become the most interesting and crucial temperatures in this study.
5.6 Fourier Transformed Infrared Spectroscopy (FTIR)

Infrared Spectroscopy was used in this study as a complementary tool to XRD for qualitatively analysing clay and non-clay minerals in the as-received and calcined samples. For a mineral, the infrared absorption originates from the vibrations of the constituent atoms while the frequencies of the vibrations totally depend on the mass of the atoms. Resembling a diffractogram, an IR spectrum can reveal structure features of a mineral. It indicates the species family that a particular mineral belongs to, and furthermore, provides information on the nature of isomorphic substituents, the differentiation between molecular water and structural hydroxyl and the degree of the regularity within that mineral (Farmer, 1968). In addition, it is worth mentioning that IR is particularly useful in distinguishing between di-octahedral and tri-octahedral species (Środoń, 2006). Compared to XRD data, an IR spectrum also contains more detailed information about amorphous phases.

The IR absorbance bands in the spectra of as-received and calcined clay samples and the corresponding assignments are given in the Table 5.4.
Table 5.4 FTIR absorbance bands and assignments (Gadsden, 1975; Madejová & Komadel, 2001; Madejová, 2003; Schroeder, 2002)

<table>
<thead>
<tr>
<th>v (cm(^{-1}))</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Kaolinite</strong></td>
<td></td>
</tr>
<tr>
<td>3696–3699</td>
<td>OH stretching of inner surface hydroxyl groups</td>
</tr>
<tr>
<td>3668–3670</td>
<td>OH stretching of inner surface hydroxyl groups</td>
</tr>
<tr>
<td>3650–3652</td>
<td>OH stretching of inner surface hydroxyl groups</td>
</tr>
<tr>
<td>3620</td>
<td>inner hydroxyl groups stretching</td>
</tr>
<tr>
<td>1114</td>
<td>perpendicular Si–O stretching</td>
</tr>
<tr>
<td>1030</td>
<td>in-plane Si–O stretching</td>
</tr>
<tr>
<td>1005–1011</td>
<td>in-plane Si–O stretching</td>
</tr>
<tr>
<td>935–940</td>
<td>in-plane bending of inner surface hydroxyl groups (AlAlOH deformation)</td>
</tr>
<tr>
<td>911–917</td>
<td>inner hydroxyl groups bending (AlAlOH deformation)</td>
</tr>
<tr>
<td>795</td>
<td>Si–O stretching</td>
</tr>
<tr>
<td>755</td>
<td>Si–O stretching</td>
</tr>
<tr>
<td>686–700</td>
<td>perpendicular Si–O stretching</td>
</tr>
<tr>
<td>530</td>
<td>Al–O–Si deformation</td>
</tr>
<tr>
<td><strong>Illite</strong></td>
<td></td>
</tr>
<tr>
<td>3630</td>
<td>inner hydroxyl groups stretching</td>
</tr>
<tr>
<td>1010–1025</td>
<td>in-plane Si–O stretching</td>
</tr>
<tr>
<td>920–927</td>
<td>inner hydroxyl groups bending (AlAlOH deformation)</td>
</tr>
<tr>
<td>825–830</td>
<td>Al–Mg–OH deformation</td>
</tr>
<tr>
<td>525</td>
<td>Al–O–Si deformation</td>
</tr>
<tr>
<td><strong>Montmorillonite</strong></td>
<td></td>
</tr>
<tr>
<td>3620</td>
<td>inner hydroxyl groups stretching</td>
</tr>
<tr>
<td>1090–1130</td>
<td>perpendicular Si–O stretching</td>
</tr>
<tr>
<td>1015–1030</td>
<td>in-plane Si–O stretching</td>
</tr>
<tr>
<td>909–920</td>
<td>inner hydroxyl groups bending (AlAlOH deformation)</td>
</tr>
<tr>
<td>625–630</td>
<td>coupled Al–O and Si–O bending, out of plane</td>
</tr>
<tr>
<td>520–540</td>
<td>Al–O–Si deformation</td>
</tr>
<tr>
<td><strong>Quartz</strong></td>
<td></td>
</tr>
<tr>
<td>1150–1170</td>
<td>Si–O stretching</td>
</tr>
<tr>
<td>796</td>
<td>Si–O stretching</td>
</tr>
<tr>
<td>778</td>
<td>Si–O stretching</td>
</tr>
<tr>
<td>692–697</td>
<td>perpendicular Si–O stretching</td>
</tr>
</tbody>
</table>
### Chapter 5 Characterization

<table>
<thead>
<tr>
<th>Water</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>3400</td>
<td>OH stretching of water</td>
</tr>
<tr>
<td>1635</td>
<td>H–O–H bending of water (OH deformation)</td>
</tr>
</tbody>
</table>
As can be seen from Table 5.4, the absorbance bands are mostly in the mid-IR frequency range (3333-333 cm\(^{-1}\)), with a minority of bands present in the near-IR frequency range (12800-3333 cm\(^{-1}\)), which are assigned to the stretching of inner-surface hydroxyl groups. The examination and interpretation of near- and mid-IR spectra of clay minerals focuses on basic constituent units within clay minerals, which includes hydroxyl groups, tetrahedral silicate and aluminate anions, octahedral metal cations and interlayer cations (Schroeder, 2002). OH stretching absorption is typically found between 3400 and 3750 cm\(^{-1}\) whilst OH bending normally lies in the region from 600 to 950 cm\(^{-1}\). The stretching modes of Si-O and Al-O are present within the 700 to 1200 cm\(^{-1}\) range, and their bending modes occur in the 150 to 600 cm\(^{-1}\) range (Schroeder, 2002). Accompanying minerals, such as quartz and feldspar, can often be identified within the range from 600 to 900 cm\(^{-1}\) and show characteristic doublet peaks (Danner, 2013).

Figure 5.11 gives the FTIR spectra of both as-received and calcined London clay samples. For as-received London clay sample, the absorption band at 3697 cm\(^{-1}\) confirms the presence of kaolinite and it is believed to originate from the in-phase symmetric stretching vibration of inner-surface hydroxyl groups (Madejová & Komadel, 2001). The absorption band at 3620 cm\(^{-1}\) that is also assigned to the stretching of inner-surface OH groups corresponds to montmorillonite and possibly illite. It is particularly typical for di-octahedral montmorillonite with a high amount of Al in the octahedral, and the exact position and shape of the peak mainly depend on the nature of the octahedral atoms to which the OH groups are coordinated (Madejová, 2003). The broad hump at 3400 cm\(^{-1}\) is due to the OH stretching of water molecules, which were partly absorbed from the air. Also the molecular water can exist in the interlayer space of montmorillonite, and therefore this absorbance band could be even more distinct for clays whose dominant constitutent is montmorillonite. In the mid-IR region, the absorption band at 1637 cm\(^{-1}\) is related to the O-H-O bending of molecular water. In the same region, there is a broad absorption peak at 993 cm\(^{-1}\) exhibiting the highest intensity and overlaying a range from about 800 to 1200 cm\(^{-1}\). It is related to the in-plane Si-O stretching of kaolinite, illite and montmorillonite, and particularly, typical for all smectites (including montmorillonite) (Madejová, 2003). On the left shoulder of the strong and wide peak, quartz shows a Si-O stretching band at 1162 cm\(^{-1}\), which is not fairly distinct on the spectrum but still observable. The absorbance at a lower
frequency of 1117 cm\(^{-1}\) reflects the perpendicular Si-O stretching of kaolinite and montmorillonite. On the right shoulder, the absorbance at 912 cm\(^{-1}\) that is assigned to inner OH groups bending (Al-Al-OH deformation) is considered typical for kaolinite, illite and montmorillonite. The Al-Mg-OH deformation band at 832 cm\(^{-1}\) confirms the presence of illite (Vaculíková & Plevová, 2005). The doublet absorption bands at 777 and 796 cm\(^{-1}\) both correspond to the Si-O stretching of quartz, and so does the single peak at 694 cm\(^{-1}\). It should be noted that the absorbance at 694 cm\(^{-1}\) also indicates the perpendicular Si-O stretching of kaolinite. In addition, one more Si-O stretching band of kaolinite is found at 752 cm\(^{-1}\). The absorbance at 523 cm\(^{-1}\) which is fairly typical for all clay minerals is assigned to Al-O-Si deformation band, reflecting the connection of tetrahedral and octahedral sheets in the clay mineral structure (Danner, 2013).

The spectra of calcined London clay samples can help explain how the crystal structure of clay minerals is altered with the increase of calcining temperature. The inner-surface OH groups stretching band of kaolinite at 3697 cm\(^{-1}\) completely disappears upon calcining at 600 °C. As the band corresponds solely to kaolinite, the disappearing can imply that kaolinite was entirely dehydroxylated at 600 °C. This is in a perfect agreement with XRD results, and further supported by the changes of several absorbance bands on the lower frequencies. The absorbance at 3620 cm\(^{-1}\) survives from calcining at 600 °C but suffers a significant decrease in intensity, and it eventually disappears at 800 °C. Since this absorbance is in fact an overlapping of the inner OH groups stretching bands of kaolinite, illite and montmorillonite, the intensity decrease at 600 °C can be explained as the result of the complete kaolinite dehydroxylation while the disappearance at 800 °C can be attributed to the complete dehydroxylation of not only kaolinite but also illite and montmorillonite. The absorption bands of molecular water at 3400 and 1637 cm\(^{-1}\) are diminished with increasing calcining temperature.

The Si-O stretching bands of quartz at 1162, 796, 778 and 694 cm\(^{-1}\) are visible at all temperatures, suggesting quartz is stable under calcination. The absorbance at 1117 cm\(^{-1}\) that is assigned to perpendicular Si-O stretching of kaolinite and montmorillonite can be observed at up to 700 °C. However, it could still exist at 800 °C as being hidden by the broad shoulder, which is based on the observation that the shoulder becomes more concave at 850 °C and higher. The previous explanation that the dehydroxylation
of kaolinite and montmorillonite finishes at different temperatures also applies here. The peak of in-plane Si-O stretching vibration band at around 993 cm\(^{-1}\) takes a slight shift to higher frequency position as the calcining temperature rises. This is considered as a result of the formation of a three dimensional amorphous silica framework (Madejová, 2003). At the lower wavenumber of 912 cm\(^{-1}\), the disappearance of the OH bending peak at all calcining temperatures is another evidence of complete dehydroxylation in the octahedral sheets of clay minerals. The absorption band at 832 cm\(^{-1}\) becomes invisible at 600 °C and above, which could confirm that, as mentioned previously, the dehydroxylation of illite starts from below 600 °C (about 550 °C).

The disappearance of the Si-O stretching band at 752 cm\(^{-1}\) along with the diminished intensity of the Si-O stretching band at 694 cm\(^{-1}\) confirms again the presence of kaolinite. It is interesting to note that the Si-O-Al bending band at 523 cm\(^{-1}\) shifts to the higher frequency upon calcining under 900 °C, and then it disappears at 900 °C and higher. Moreover, when under 900 °C, the strongest intensity is found at 800 °C. Wang et al (2002) suggested that the shift on frequency may imply a change in the bond length. At 600 °C, although kaolinite is completely transformed into metakaolin, illite and montmorillonite are not fully dehydroxylated. However, the Si-O-Al bond length could have been changed due to the incomplete removal of OH groups in the octahedral sheets of illite and montmorillonite, which causes the absorbance a slight shift to the higher frequency. It is the same case for 700 °C but the absorbance gains an increase in intensity instead of taking a further shift. At 800 °C, all the OH groups in the octahedral sheets of illite and montmorillonite could be removed as the shifted band exhibits higher intensity than in any other calcined clay spectrum. The intensity is then diminished at 850 °C, followed by the complete disappearing of the band at 900, 950 and 1000 °C, which can reflect a decreasing amount of octahedral cations (Madejová, 2003). This may indicate that structural alteration more influential and destructive than dehydroxylation is introduced to illite and montmorillonite at 850 °C, and the original Si-O-Al bond is no longer present at 900 °C and above. The Si-O-Al bond serves as a bridge to connect the tetrahedral sheet and the octahedral sheet in clay minerals, and it is therefore further confirmed that the dehydroxylation of illite and montmorillonite takes place at around 600 °C without causing significant impact on the crystallinity, and the crystalline phase can be completely transformed into the amorphous phase when the temperature reaches at least 900 °C.
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There is no outstanding difference found between the spectra of 900, 950 and 1000 °C. Although the occurrence of recrystallization is recognizable at 950 and 1000 °C on the diffractogram, nothing relevant is observed on the corresponding IR spectra. However, the information on the amorphization of clay minerals with increasing calcination temperature reflected by IR spectra is, overall, in excellent agreement with that by XRD data.
Figure 5.11 FTIR data of as-received and calcined clay samples
5.7 Thermogravimetric analysis (TGA/DTG)

TGA/DTG is a particularly useful technique in characterizing clay materials, because it can simultaneously monitor and record the weight loss development of clays with increasing temperature. For clay minerals, the dehydroxylation process that causes weight loss occurs within various temperature ranges, depending mainly on their layered structures and the amount of contained hydroxyl groups. Studying the correlation between weight loss and temperature range on TGA/DTG curves allows researchers to conduct qualitative and quantitative analysis on the constituent clay minerals. In this study, the TGA/DTG data of as-received London clay is shown in Figure 5.12.

![TGA/DTG data of as-received London clay](image)

**Figure 5.12** TGA/DTG data of as-received London clay

On the DTG curve of as-received clay sample, the first peak (I) spanning the temperature range 50 ~ 150 °C can correspond to the removal of absorbed free water. Also it should be associated with the elimination of the water molecules located in the interlayer space of montmorillonite. As the temperature rose rapidly at 15 °C/min, a broader and much more intense peak (II) appears between around 350 and 650 °C. It
can be mainly attributed to the dehydroxylation of kaolinite, illite and montmorillonite. However, individual contribution to the peak $II$ may vary among the three clay minerals, and kaolinite can be the largest one. Kaolinite can be completely dehydroxylated at 600 °C, because no sign of kaolinite is observable on the XRD and FTIR spectra of 600 °C calcined clay sample. Furthermore, as previously discussed in FTIR results analysis, the dehydroxylation of illite and montmorillonite starts from below 600 °C and finishes at higher than 800 °C. Both 2:1 clay minerals are therefore responsible for not only the second peak ($II$) but the third peak ($III$). Some of the accompanying minerals, such as chlorite and pyrite, are also decomposable under 1000 °C, but their contribution to this weight loss development is believed to be minor.

TGA/DTG measurements were also carried out for calcined clay samples. Particular attention is paid to 350 ~ 1000 °C, which covers typical dehydroxylation temperature ranges for all the studied clay minerals. The DTG data of as-received and calcined clay samples within 350 ~ 1000 °C is given in Figure 5.13.

![Figure 5.13 DTG data of as-received and calcined clay samples within 350~1000 °C](image)

It is manifest in Figure 5.13 that upon calcination at 600 °C, the peak $II$ almost disappears, leaving only a fairly small hump, while the peak $III$ seems to be unaffected.
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For all the clay samples calcined at higher than 600 °C, the peak II is missing. Moreover, a gradual decrease in peak III intensity can be clearly observed on the curves (700, 800, 850 and 900 °C), and a complete disappearance of peak III happens to 950 and 1000 °C calcined clay samples.

In general, the thermogravimetric behavior of as-received and calcined clay samples is consistent with the findings from XRD and FTIR analyses. Kaolinite can be considered as being completely dehydroxylated and transformed into meta-phase at 600 °C while illite and montmorillonite need a higher temperature (above 800 °C) to expel all the hydroxyl groups bonded in the octahedral layers and cause a collapse to the whole layered structure.

The temperatures from 350–950 °C includes all typical temperature ranges for dehydroxylation of the clay minerals. Figure 5.14 introduces the dehydroxylation degree of as-received London clay, which is calculated from the weight loss within 350–950 °C. It was reported that complete dehydroxylation, theoretically, can cause pure kaolinite a weight loss of 13.9% on a dry weight basis, and the figure for illite and montmorillonite is 5%. (Earnest, 1988; Todor, 1976). Assuming that nothing other than the three clay minerals is contributory to the weight loss within 350–950 °C and the dehydroxylation temperatures do not overlap, it can be estimated from Figure 5.14 that kaolinite accounts for ~30.2 wt.% of the as-received London clay whilst illite and montmorillonite comprise ~53.2 wt.%.
Figure 5.14 The dehydroxylation degree of as-received London clay (350–950 °C)
5.8 Inductively coupled plasma optical emission spectroscopy (ICP-OES)

ICP-OES technique was applied to determine the ion release of as-received and calcined London clay samples in water. Particular attention is paid to these elements, Al, Si, Ca, Na, Mg, K and Fe. The pH of tested solutions was measured as well. All results are shown in Table 5.5.

Table 5.5 Ion release of as-received and calcined clays in distilled water

<table>
<thead>
<tr>
<th>Materials</th>
<th>Al (mg/l)</th>
<th>Si (mg/l)</th>
<th>Ca (mg/l)</th>
<th>Na (mg/l)</th>
<th>Mg (mg/l)</th>
<th>K (mg/l)</th>
<th>Fe (mg/l)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-received</td>
<td>0.0</td>
<td>9.5</td>
<td>26.7</td>
<td>4.2</td>
<td>13.2</td>
<td>12.5</td>
<td>0.0</td>
<td>5.4</td>
</tr>
<tr>
<td>clay</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>600 °C CLC</td>
<td>0.0</td>
<td>18.5</td>
<td>47.8</td>
<td>5.1</td>
<td>49.2</td>
<td>31.6</td>
<td>0.0</td>
<td>6.0</td>
</tr>
<tr>
<td>700 °C CLC</td>
<td>0.0</td>
<td>13.6</td>
<td>49.4</td>
<td>3.8</td>
<td>54.3</td>
<td>21.1</td>
<td>0.0</td>
<td>6.5</td>
</tr>
<tr>
<td>800 °C CLC</td>
<td>0.0</td>
<td>7.6</td>
<td>42.6</td>
<td>2.2</td>
<td>39.1</td>
<td>15.6</td>
<td>0.0</td>
<td>7.1</td>
</tr>
<tr>
<td>850 °C CLC</td>
<td>0.0</td>
<td>4.0</td>
<td>20.6</td>
<td>0.9</td>
<td>9.2</td>
<td>12.2</td>
<td>0.0</td>
<td>7.6</td>
</tr>
<tr>
<td>900 °C CLC</td>
<td>0.1</td>
<td>3.6</td>
<td>12.7</td>
<td>1.0</td>
<td>4.3</td>
<td>9.0</td>
<td>0.0</td>
<td>7.7</td>
</tr>
<tr>
<td>950 °C CLC</td>
<td>0.3</td>
<td>4.1</td>
<td>7.4</td>
<td>0.9</td>
<td>2.7</td>
<td>5.1</td>
<td>0.1</td>
<td>7.8</td>
</tr>
<tr>
<td>1000 °C CLC</td>
<td>0.6</td>
<td>4.5</td>
<td>4.9</td>
<td>0.5</td>
<td>1.8</td>
<td>3.5</td>
<td>0.2</td>
<td>7.7</td>
</tr>
</tbody>
</table>

- CLC = calcined London clay

The pH is increased from 5.4 to 6.0 upon calcining at 600 °C, the lowest studied temperature. It then continues to gradually rise with the increasing calcining temperature to up to 900 °C, and becomes relatively stable at 900, 950 and 1000 °C. There are only minor soluble Al and Fe in water across the calcining temperature range while the release of Si, Ca, Na, Mg and K into water is considerably affected by different calcining temperatures. It is indicated by XRF analysis results that Al$_2$O$_3$ and Fe$_2$O$_3$ account for 12.8 and 7.7 wt.% of as-received London clay, respectively.
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However, it seems that neither crystalline nor amorphous alumina is water soluble in this study. Iron can be from pyrite and goethite, as the presence of both in the as-received clay is confirmed by XRD. Iron may also exist in the 2:1 clay minerals, such as montmorillonite and illite, acting as the cations in the octahedral layers. It is well understood and recognized that the iron content easily gets oxidized to hematite upon calcination, which is insoluble in water. This may explain the extremely low Fe release in water in both as-received and calcined forms.

As shown in Table 5.5, calcining can make greater impact on the ion release of Si, Ca, Na, Mg and K, compared to Al and Fe. Figure 5.15 illustrates how the pH and the ion release of Si and Na change with increasing calcining temperature, while Figure 5.16 shows that of Ca, Mg and K.

![Figure 5.15](image.png)

**Figure 5.15** Ion release of Si and Na in water for as-received and calcined clays (some error bars are invisible because they are smaller than the used data symbols)
Both Si and Al are associated with pozzolanic reaction but their behaviours on the ion release in water in this case differ significantly. The water soluble Si is higher under all the studied conditions (uncalcined and calcined) than the water soluble Al. This can possibly be explained from the differentiation of locations within 2:1 clay minerals between Si and Al. The tetrahedral Si is more exposed to the environment as compared to the octahedral Al because each octahedral layer within 2:1 clay minerals is packed between two adjacent tetrahedral layers. The dissolution is therefore far more likely to happen to the tetrahedral Si. Additionally, such a finding could also indicate that the substitution of Al to Si in the tetrahedral layers is minor or negligible. The highest amount Si release is found to be with 600 °C calcined clay sample, and subsequently, the amount decreases sharply until 850 °C, from which it becomes relatively stable. It is interesting to note the decrease in the amount of water soluble Si within the calcining temperature range 600 ~ 850 °C. The increasing pH may be the main factor limiting the dissolution of amorphous silica.

Because there are no Ca(OH)$_2$ and CaCO$_3$ present in the as-received London clay, as confirmed by XRD and FTIR analysis, the existing Ca is most likely from the
interlayer space of montmorillonite. Na derives from the same source as Ca. These cations can be easily freed from the interlayer space of montmorillonite into water. For the 600 and 700 °C calcined clay, the shift of the montmorillonite (001) reflection from 6.2 to 8.9 °2θ on the XRD spectra indicates the interlayer space has been affected by heating. And this phenomenon may further facilitate the dissolution of Ca and Na from the interlayer space, which results in the increased Ca and Na concentrations in water. However, a dropping trend in ion concentration at following temperatures can be observed for Ca as well as Na. FTIR analysis results suggest the further heating-induced structural alteration to montmorillonite within the range of 800–1000 °C, including the completion of dehydroxylation at 800 °C and the collapse of the whole layered structure at 850 °C and higher. The interlayer space is shrunk and eventually no longer present as the calcining temperature increases from 800 to 1000 °C. This might cause Ca and Na to diffuse into meta-phase, which prevents them from the dissolution in water. On the other hand, the substantial drop of Ca\(^{2+}\) concentration may also be attributed to the increase in pH from below 7.0 to above.

In the as-received London clay, Mg is derived from the brucite layer of chlorite as well as the octahedral layer of illite and montmorillonite. The growing ion release upon calcining at 600 and 700 °C could be caused by the dissolution of the dehydroxylated brucite layer of chlorite. The octahedral magnesium cation in the illite and montmorillonite may also contribute to the measured concentration. The significant drop in concentration starting from 850 °C is possibly due to the increased pH as well as the structural collapse of illite and montmorillonite that traps the octahedral cations into the meta-phase and consequently prevents them from escaping (Danner, 2013). To explain the fairly low Mg\(^{2+}\) concentration at 950 and 1000 °C, the recrystallization of spinel could also be taken into consideration (Garg & Skibsted, 2016).

Illite and K-feldspar are the main source of K in the as-received London clay. The ion release behaviour of K in water follows a similar way to that of Na. At the temperatures higher than 900 °C, the low K\(^{+}\) concentration can also be attributed to the amorphous meta-phase, which impedes the dissolution of K in water (Danner, 2013).
5.9 BET surface area and porosity

Surface area of particles is another important parameter in studying and understanding the properties of SCMs. It is directly determined by particle fineness as well as particle porosity. In this study, nitrogen gas adsorption technique was employed to carry out the measurements of BET surface area and porosity for all different materials.

The BET surface areas of as-received clay, calcined clays, PFA, GGBS, Silica fume and ground sand are reported in Table 5.6. It should be noted that all the calcined clay samples were re-ground prior to the measurements.

**Table 5.6 BET surface area measurement results**

<table>
<thead>
<tr>
<th>Materials</th>
<th>BET surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-received clay</td>
<td>45.1 (± 0.17)</td>
</tr>
<tr>
<td>600 °C CLC</td>
<td>18.5 (± 0.08)</td>
</tr>
<tr>
<td>700 °C CLC</td>
<td>16.9 (± 0.07)</td>
</tr>
<tr>
<td>800 °C CLC</td>
<td>13.7 (± 0.04)</td>
</tr>
<tr>
<td>850 °C CLC</td>
<td>7.8 (± 0.02)</td>
</tr>
<tr>
<td>900 °C CLC</td>
<td>5.6 (± 0.02)</td>
</tr>
<tr>
<td>950 °C CLC</td>
<td>3.5 (± 0.02)</td>
</tr>
<tr>
<td>1000 °C CLC</td>
<td>2.2 (± 0.02)</td>
</tr>
<tr>
<td>PFA</td>
<td>2.7 (± 0.01)</td>
</tr>
<tr>
<td>GGBS</td>
<td>1.5 (± 0.02)</td>
</tr>
<tr>
<td>Silica fume</td>
<td>25.1 (± 0.06)</td>
</tr>
<tr>
<td>Ground sand</td>
<td>2.1 (± 0.01)</td>
</tr>
</tbody>
</table>

- CLC = calcined London clay

For all the calcined clay samples, despite the consistency in particle fineness, owing to the second grinding as previously depicted in Section 5.3, the BET surface area varies significantly. It shrinks with the increasing calcining temperature, as shown in Table 5.6. The phenomenon can imply that the higher the calcining temperature, the lower the porosity of calcined clay samples. The most substantial reduction in the BET surface area (from 13.7 to 7.8 m²/g) is found between 800 and 850 °C. As suggested in Section 5.6, FTIR analysis results indicate that the dehydroxylation of illite and
montmorillonite may complete at 800 °C whilst structural alteration that is more destructive than dehydroxylation may happen to illite and montmorillonite at 850 °C and higher. It is therefore likely that the considerable decrease in BET surface area is associated with the heat-induced structural alteration or distortion of illite and montmorillonite at 850 °C.

Danner (2013) emphasized that the layered crystal structures enable clay minerals to have huge specific surface area, and it is particularly typical for montmorillonite that the inner or inter-crystalline surface is found to be larger than outer surface. In his work, a Denmark clay, where montmorillonite is in abundance, exhibits the same trend on BET surface area with the increasing calcining temperature. The gradual decrease in BET surface area upon calcining at and under 700 °C is attributed to an initial collapse of the structural layers through dehydration of the interlayer spaces reducing the d-spacing of the mineral structure. The significant drop in BET surface area at 850 °C is the indication of a further decrease of inner surfaces, resulting from a more intense structural transformation.

Porosity analysis was performed for all the materials, helping better explain the observed changes in BET surface area with the increasing calcining temperature. According to the classification of pores recommended by The International Union of Pure and Applied Chemistry (IUPAC), pores can be divided into three categories, depending on their size. The pores with a size lower than 2 nm are referred to as micropores, while the pores with a size above 50 nm are referred to as macropores. Additionally, the pores in between micropores and macropores are referred to as mesopores. It is important to understand clay structural units prior to the origins of micropores, mesopores and macropores in a clay mineral. The first and fundamental unit is elementary layer (clay platelet about 1 nm thick), and the second is tactoid (2 ~ 50 nm), which is a turbostratic stacking of parallel clay platelets (Kleijn & Oster, 1982). The turbostratic stacking results from random rotations and translations between adjacent elementary layers (Cases et al, 1992). The last unit is aggregate (up to 1 µm), consisting of tactoids. The type of arrangement of tactoids within aggregates can vary, depending on the exchanged cation (Neaman, Pelletier & Villieras, 2003). Kuila & Prasad (2013) introduced the multiple scales of pore structures within clay minerals. Intra-tactoid pores (~ 3 nm, classified as micropores or fine mesopores) are associated with the slit-shaped or wedged pores on the broken edges of turbostratic stacking of
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elementary layers within tactoids. Inter-tactoid pores (20 ~ 100 nm, classified as large mesopores or fine macropores) are formed by stacking tactoids within an aggregate. Inter-aggregate pores (classified as macropores) are usually in the micron size range, originating from stacking aggregates with preferred alignment.

Nitrogen gas adsorption experiments provide gas-adsorption isotherms, which can be used to qualitatively analyse the types of pores within adsorbents. According to the classification from IUPAC, gas-adsorption isotherms are divided into six types (Type I, II, III, IV, V and VI), and hysteresis patterns on the isotherms are divided into four types (Type H1, H2, H3 and H4). All these types are presented in the Appendix. The nitrogen gas adsorption-desorption isotherms of the test materials in this study are shown in Figure 5.17.
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(e) 850 °C calcined clay - Adsorption
(f) 900 °C calcined clay - Adsorption

(g) 950 °C calcined clay - Adsorption
(h) 1000 °C calcined clay - Adsorption

(i) PFA - Adsorption
(j) GGBS - Adsorption
Figure 5.17 Adsorption-desorption isotherms of the test materials: a) as-received clay, b) 600 °C, c) 700 °C, d) 800 °C, e) 850 °C, f) 900 °C, g) 950 °C, h) 1000 °C calcined clay, i) PFA, j) GGBS, k) silica fume and l) sand

Figure 5.17 i), j), k) and l) show that the adsorption-desorption isotherms of PFA, GGBS, silica fume and ground sand exhibit minor and insignificant hysteresis and almost reversible adsorption-desorption branches. They can therefore be correlated with Type II isotherm, which suggests macropores are dominant in those materials.

The isotherm of as-received clay significantly differs from them, and it does not match any IUPCA-suggested type (from Type I to VI) in terms of the shape. The higher adsorption at low $P/P_0$ indicates as-received clay contains more micropores than PFA, GGBS, silica fume and ground sand. The presence of mesopores is confirmed by the observed H3 hysteresis whilst the absence of a Type IV-like plateau at high relative pressure (near to 1.0) could suggest the existence of macropores. In addition, the particular H3-type hysteresis pattern indicates the mesopores are slit-like. The ‘forced closure’ of the desorption branch at $0.4<P/P_0<0.5$ is because of the ‘tensile strength effect’, which indicates the huge quantity of fine mesopores with a diameter less than 4 nm (Kuila & Prasad, 2013). For the calcined clay samples, the hysteresis is reduced with the increasing calcining temperatures. The hysteresis becomes extremely narrow when the calcining temperature is 850 °C. Further distinctive change can be observed at 1000 °C, as the hysteresis almost disappears, leaving reversible adsorption-desorption branches.
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By applying the BJH (Barret, Joyner and Halenda) method on the adsorption isotherms, the pore size distribution of as-received and calcined clay samples is obtained, as shown in Figure 5.18.

![BJH pore size distribution of as-received and calcined clays (V: pore volume; D: pore diameter)](image)

**Figure 5.18** BJH pore size distribution of as-received and calcined clays (V: pore volume; D: pore diameter)

As illustrated in Figure 5.18, calcining can cause a significant impact on the pore size distribution of clay samples. Neaman, Pelletier & Villiers (2003) suggested that calcining could lead to collapse of the layers and tactoids, and therefore porosity may become inaccessible for nitrogen molecules. The volume of fine macropores is found to increase after as-received clay is calcined at 600, 700, 800 and 850 °C. The volume of micropores and fine mesopores is considerably decreased upon calcining at all the studied temperatures. The higher the calcining temperature, the lower the volume of micropores and fine mesopores, or the less the micropores and fine mesopores, which corresponds to the finding of BET surface area analysis. Furthermore, the most distinctive decrease is unsurprisingly observed between 800 and 850 °C. At 950 and 1000 °C, there are almost no micropores and fine mesopores present, which indicates the two samples can be considered as macroporous.

Based on the above results and discussion, 850 °C is found to be the most important temperature in explaining the impact of calcining on the particle surface area and
porosity of London clay. The reported behaviour of clay samples is particularly typical for montmorillonite. Although as-received London clay is in fact a mixture of various clay and non-clay minerals, montmorillonite dominates in the porosity measurement results. Structural distortion that is more intense and destructive than dehydroxylation happens to montmorillonite at 850 °C, which is possibly responsible for the significant drop of BET surface area and porosity from 800 to 850 °C.
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5.10 Isothermal conduction calorimetry

Isothermal conduction calorimetry was used to study the early hydration, up to 48 hours, of the cement pastes containing calcined London clay, PFA, silica fume and silica sand. It is well known that the heat evolution of ordinary Portland cement (CEM-I) hydration is divided into five typical periods or stages, as illustrated in Figure 5.19.

The five typical heat evolution periods associated with CEM-I hydration reaction are recognized as follows:

I) the initial reaction period (typically as short as several minutes);
II) the induction period (typically 1~2 hours);
III) the acceleratory period (typically ~8 hours);
IV) the deceleratory period (typically 8~20 hours);
V) the slow reaction period.

The reaction kinetics behind each period, as well as the causes of each peak, has been well investigated and discussed by previous researchers (Neville, 1996; Taylor,
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1997). Their work facilitates the interpretation of hydration heat developments of different blended cement pastes in this study.

For all the involved pastes, the rate of heat evolution in 48 hours is shown in Figure 5.20 a), and Figure 5.20 b) scales up the first 0.2 hours for a clearer presentation of the initial reaction period and the induction period. The cumulative hydration heat over 48 hours is illustrated in Figure 5.21 a), whilst the cumulative heat development corresponding to Figure 5.20 b) is presented in Figure 5.21 b). The binder on the y-axis of each figure means CEM-I plus a test material.

a) from 0 to 48 hours

![Heat evolution diagram](image-url)
b) from 0 to 0.2 hours

Figure 5.20 Rate of hydration heat evolution of blended cement pastes: a) from 0 to 48 hours; b) from 0 to 0.2 hours

a) from 0 to 48 hours
b) from 0 to 0.2 hours

![Cumulative hydration heat of blended cement pastes](image.png)

**Figure 5.21** Cumulative hydration heat of blended cement pastes: a) from 0 to 48 hours; b) from 0 to 0.2 hours

It is interesting to note that when mixed with CEM-I and water at the same ratio, calcined clay samples caused substantially different impacts on the hydration heat evolution, depending on the calcining temperatures.

As shown in the Figure 5.20 b), during the initial reaction period, the paste containing 600 °C calcined clay sample exhibits the highest heat development rate, followed by the pastes representing 800 and 700 °C. The control paste that is comprised of only CEM-I and water releases less heat than the above three pastes but considerably more than any other paste involved in this measurement. It is well understood that the peak in the initial reaction period can be attributed to a combination of different effects, including the exothermic wetting of cement particles, the hydration of calcium sulphate hemihydrate to dihydrate gypsum and the hydration of C₃A to ettringite (Taylor, 1997; Mostafa & Brown, 2005). In comparison with the control paste, the peak intensities of the pastes (900 °C, 950 °C, 1000 °C, PFA, silica fume and sand) are decreased, which results from the dilution effect. The increased initial hydration heat of the pastes (600 °C, 700 °C and 800 °C) is possibly due to the additional reactive amorphous
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alumina in those calcined clay samples, which can stimulate the hydration of C\textsubscript{3}A and the formation of ettringite (Danner, 2013). Although the dilution effect works in this case as well, the heat from the promoted C\textsubscript{3}A hydration and ettringite formation is much greater so that the overall heat release exceeds that of the control paste. The additional amorphous alumina originates from the transformation of kaolinite to metakaolin. For the clay samples calcined at higher than 800 °C, the recrystallization of spinel (MgOAl\textsubscript{2}O\textsubscript{4}) had taken place during calcining, which significantly reduced the amount of amorphous alumina deriving from the formation of metakaolin. The occurrence of recrystallization of spinel is recognized and confirmed on the XRD pattern of 950 and 1000 °C calcined clay samples. As a result of the recrystallization, the dilution effect may become prevailing in those pastes. There is another possible reason that could explain the heat evolution differences between pastes in the initial reaction period. Although no distinct variation on particle size is present amongst all the calcined clay samples, the particle surface areas, determined by the BET method, are 18.5, 16.9, 13.7, 5.6, 3.5 and 2.2 m\textsuperscript{2}/g for 600, 700, 800, 900, 950 and 1000 °C calcined clays, respectively. It is evident that the higher the calcining temperature, the lower the surface area. The most significant reduction (from 13.7 to 5.6 m\textsuperscript{2}/g) takes place when the temperature rises from 800 to 900 °C. It coincides with the noticeable reduction on the intensity of the first heat evolution peak, from above that of control paste at 800 °C to below at 900 °C. The coincidence may imply that surface area can cause a considerable impact on the heat evolution of early hydration, and particularly, higher surface area can make clay particles more exposed to the surrounding environment when acting as nucleation sites to facilitate the hydration of C\textsubscript{3}A. Though the hydration heat released from the pastes during the initial reaction period varies greatly, the time of occurrence of the first peak maxima is relatively stable.

During the induction period, as can be seen in the Figure 5.20 a), the highest rate of heat evolution is still exhibited by the one representing 600 °C calcined clay, which is followed by 700 °C and 800 °C. This is in a good agreement with the descending order of surface area. Apart from the three, the only one showing higher rate than the control paste during this period is the paste incorporating silica fume. All other pastes generated less heat than the control paste, due to the dilution effect. In addition, the time of occurrence of the valley minima is increased for all the blended cement pastes.
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The induction period is followed by the acceleratory period and the deceleratory period, both of which constitute the second peak on the heat evolution rate curve. It is well understood that the second peak on the curve is mainly attributed to the hydration of C₃S and C₂S. As shown in the Figure 5.20 a), the time of occurrence of the second peak maxima is decreased for the pastes containing 600, 700 and 800 °C calcined clays, which is an indication that the three calcined clay samples can accelerate the hydration of C₃S and C₂S. This could be also due to the higher particle surface areas that enable them to work more efficiently as nucleation sites for hydration products. For the three calcining temperatures, it is also interesting to note that a third peak that closely follows the second peak appears on each curve. The third peak in CEM-I hydration heat evolution is, in literatures, normally attributed to the conversion of AFt (ettringite, trisulfate) to AFm (monosulfate) phases and the renewed formation of ettringite (Neville, 1996; Taylor, 1997). However, there is no third peak present on the curve of the control paste which is prepared from mixing CEM-I with water only. The absence indicates that there could be no conversion of AFt to AFm at all in the control paste, or the converted amount is possibly too low to avoid being hidden within the uncertainty of the experimental method (Tydlitát, Zákoutský & Černý, 2014). According to XRF analysis results, London clay contains higher alumina content than the CEM-I used in this study. In the binary mixes of the calcined London clay (600, 700 and 800 °C) and the CEM-I, due to the higher alumina content in the calcined clay, the SO₃/Al₂O₃ molar ratio is reduced, which is in favour of the conversion of AFt to AFm phases and therefore results in a pronounced third peak on each of the three curves. As discussed previously, in this calorimetry measurement 800 °C is the highest temperature that can transform kaolinite, where alumina is present in a crystalline state, into metakaolin, where reactive amorphous alumina can be found, without causing the recrystallization of amorphous alumina to spinel. Also crystalline alumina within calcined clay samples is possibly unable to contribute to the conversion of AFt to AFm. This might well explain why there are no such peaks found on the curves representing 900, 950 and 1000 °C. The time of occurrence of the second peak maximum on the silica fume curve is decreased, which may also result from the higher particle surface area, and the curve does not show a similar AFt-to-AFm conversion peak. For the other curves (900 °C, 950 °C, 1000 °C, PFA and sand), the time of occurrence of the second peak maxima is not considerably altered, and no AFt-to-AFm conversion
peaks are present. Moreover, due to the persistent dilution effect, no curve amongst all exhibits higher intensity for the second peak than the control paste curve.

During the deceleratory period, after about 15 hours, the curves without the AFt-to-AFm conversion peak exhibit a broad shoulder. This shoulder is attributed to the pozzolanic reaction of the test material and the relatively high concentration of Ca(OH)$_2$ formed after the main C$_3$S and C$_2$S hydration peak (Mostafa & Brown, 2005). The presence of the shoulder, therefore, may indicate that pozzolanic reaction is more influential in the hydration heat evolution for PFA, silica fume, 900 °C, 950 °C and 1000 °C calcined clays than for 600 °C, 700 °C and 800 °C calcined clays. This is in accordance with the results of pozzolanic reactivity assessment, which will be discussed in details in the next Chapter. In addition, it is surprising that, from about 17 hours to 30 hours, the paste incorporating sand exhibits a higher rate of heat evolution than any of the pastes incorporating 600 °C, 700 °C and 800 °C calcined clays. That is probably because the C$_3$S and C$_2$S hydration of calcined clay blended pastes is accelerated, as mentioned earlier. Moreover, quartz, which is the predominant constituent of the sand, can stimulate the hydration of CEM-I by causing more Ca(OH)$_2$ to form (Rahhal & Talero, 2008). This might also contribute to the surprisingly high rate of heat evolution found on the sand curve between 17 to 30 hours. The dilution effect works throughout this period and the following slow reaction period for every blended cement paste.

The cumulative hydration heat development is presented in the Figure 5.21 a) and b). It is manifest that the blended cement pastes containing 600 °C, 700 °C and 800 °C calcined clays release more heat than any other paste in the first approximate 13 hours, and they are completely overtaken by the control paste afterwards. The sand-CEM-I blended paste is unsurprisingly the least one at the very late age on the figure.

The behaviour of PFA and silica fume in the calorimetry measurement is overall in agreement with the findings in literatures (Cheng-yi & Feldman, 1984; Mostafa & Brown, 2005; Snelson, Wild & O’Farrell, 2008; Vance et al, 2013).
5.11 Discussions

Characterization was performed on all test materials. As determined by XRD, London clay is a complex mix of various clay minerals (kaolinite, illite, montmorillonite and chlorite) and accompanying minerals (quartz, feldspar, pyrite and goethite). Calcining at certain temperatures can cause London clay significant compositional and structural changes, including oxidation, dehydration, dehydroxylation, amorphization and recrystallization.

The oxidation of iron(II) to iron(III) by calcining is typically observed for naturally-formed Fe-bearing materials. In this study, it is suggested by XRF analysis that iron oxide comprises ~7.7 wt.% of as-received London clay, which is the third largest percentage, only less than ~45.8 wt.% for SiO$_2$ and ~12.8 wt.% for Al$_2$O$_3$. Therefore the oxidation state change of iron(II) to iron(III) is particularly recognizable by the colour change of dark/grey for uncalcined to brown/red for calcined. Moreover, the formation of hematite due to calcining has been confirmed by observing relevant reflections on the XRD patterns of all calcined clay samples. The dehydration refers to the removal of water molecules located in the interlayer space of 2:1 clay minerals as well as free water absorbed from the atmosphere. The shift of the basal plane (001) reflection from 6.2 to 8.9 °2θ is a sign for montmorillonite that the interlayer space water was driven off as a results of calcining. As compared to dehydration, dehydroxylation requires more intensive heating. Kaolinite can lose all hydroxyl groups chemically bonded in octahedral sheets when calcined at 600 °C. This allows a complete collapse to its original 1:1 structure, leading to the formation of amorphous phase metakaolin. For 1:1 structured kaolinite, dehydroxylation can be considered identical to amorphization in the context of calcining. However, it is not the case for the studied 2:1 clay minerals. For illite and montmorillonite, FTIR data analysis suggests that dehydroxylation may start from below 600 °C, and finish at ~800 °C. Further evidences provided by XRD and FTIR, particularly the Si-O-Al bending band at 523 cm$^{-1}$, demonstrate that neither of 2:1 clay minerals suffered substantial decrease in crystallinity from the heat-induced removal of octahedral hydroxyl groups. The complete disappearing of those characteristic reflections and absorptions occurs in 900–950 °C calcined clays, and hence it is believed that in those samples illite and montmorillonite were structurally distorted and entirely transformed into amorphous
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phase. This means dehydroxylation is only a part of amorphization process in the case of 2:1 clay minerals. Recrystallization should be avoided during calcining, as it is unfavourable to extracting the best out of London clay in terms of pozzolanic reactivity. The two peaks appearing at 37.1 and 65.4 °2θ confirm the occurrence of recrystallization of spinel in 950 and 1000 °C calcined clays.

In TGA data analysis, the ‘dehydroxylation degree’ of as-received London clay was introduced in Figure 5.14 with two assumptions: no substance other than kaolinite, illite and montmorillonite contributes to the weight loss occurring within 350~950 °C; there is no overlapping in dehydroxylation temperature ranges between kaolinite (considered as 350~600 °C) and illite/montmorillonite (considered as above 600 °C). Despite the previous conclusion that dehydroxylation is not necessarily equivalent to amorphization, particularly in the case of 2:1 clay minerals, the ‘dehydroxylation degree’ can still somewhat serve as an indicator for the amount of amorphous phase contained in calcined clays, which will be used in next chapter to discuss the effect of calcining at different temperatures on the pozzolanic reactivity.

It is known that clay particles would become agglomerated on calcining at sufficiently high temperatures due to sintering, and Figure 5.2 demonstrates the degree of agglomeration can evolve favourably as calcining temperature increases. In this work, all calcined clay samples were re-ground for a fixed time to achieve a better homogeneity in particle fineness. In addition, the measured BET surface areas vary significantly among the re-ground calcined clay samples. Figure 5.22 presents the correlation between particle fineness ($d_{50}$) and BET surface area for all test materials.
Figure 5.22 Correlation between particle fineness (d50) and BET surface area

It is clear that BET surface area drops largely upon calcining at 600 °C and it continues to decline as the calcining temperature is raised. Also it is unsurprising to find out from Figure 5.22 that for calcined clays, BET surface area is uncorrelated with particle fineness. This is primarily because London clay particles are porous, and calcining at 600~1000 °C can effectively reduce the porosity of London clay particles by causing structural collapse to the clay minerals.
Chapter 6 POZZOLANIC REACTIVITY ASSESSMENT
6.1 Frattini test

Frattini test is a well-established method to assess pozzolans in terms of their portlandite fixation ability. As its process involves Portland cement, letting portlandite in the system be formed from cement hydration rather than added manually as a chemical, it enables pozzolans to participate in pozzolanic reaction under a condition that more resembles a real practice of blended cement. It is understood that the solubility of portlandite is largely dependent on the temperature. A solubility curve of portlandite/lime at 40 °C is employed to differentiate the pozzolanic area from its non-pozzolanic counterpart on the figure, where Frattini test data is presented as CaO, equivalent to Ca$^{2+}$, in mmol/l on the y-axis against OH$^{-}$ in mmol/l on the x-axis. It is therefore crucial to keep the oven temperature unchanged at 40 °C before samples are tested.

All the studied materials including calcined clays, PFA, silica fume and GGBS were tested, following the procedures specified in BS EN 196-5. Silica sand is also involved, as an inert material to be compared with others. The test time was selected as 8 and 15-day, the results of which are shown in Figure 6.1 and 6.2, respectively.
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Figure 6.1 Frattini test results on the 8-day

Figure 6.2 Frattini test results on the 15-day
As shown in Figure 6.1, 600 and 700 °C calcined clay samples are located above the solubility curve of portlandite, which indicates that both samples are not rather pozzolanic on the 8-day. In contrast, all the other calcined clay samples (800, 850, 900, 950 and 1000 °C) are present below the portlandite solubility curve after 8 days, which implies they are more reactive on fixing portlandite generated from cement hydration. Additionally, silica fume can be found far below the solubility curve, exhibiting a highly reactive character, and PFA is determined to be located in the pozzolanic area with a close proximity to 850 °C calcined clay in Figure 6.1. Sand, considered inert in terms of reacting with portlandite, lies in the non-pozzolanic area. However, it is worth noting that GGBS, unlike silica fume and PFA, was determined to be situated within the non-pozzolanic area, showing a considerable distance from the solubility curve in Figure 6.1. The control sample, which contains no SCM replacement, also lies above the curve after 8 days.

It is shown in Figure 6.2 that on the 15-day, 600 and 700 °C calcined clay samples remain to lie in the non-pozzolanic area, and so does sand as well as the control sample. The clays calcined at 800, 850, 900, 950 and 1000 °C remain staying in the pozzolanic area, which is predictable and reasonable. PFA and silica fume were also determined to lie in the pozzolanic area in Figure 6.2, while GGBS was still located above the portlandite solubility curve.

In the comparison between Figure 6.1 and 6.2, corresponding to the 8-day and 15-day respectively, there is no inter-area change in location, preferably from non-pozzolanic to pozzolanic area, observed for any studied sample. However, as the curing age increased, a downward movement towards x-axis is commonly seen for most samples. Furthermore, the downward movement of samples varies in extent, as mentioned previously.

Frattini test results are normally reported in a diagrammatic way as specified in BS EN 196-5, like Figure 6.1 and 6.2. They can clearly tell whether or not a specific material is pozzolanic by examining its position relative to the defined boundary (the portlandite solubility curve). However, it is difficult to correlate them with the results of other pozzolanic reactivity testing methods. It is therefore necessary to quantify the Frattini test results. This can be achieved by considering the distance of data points from the portlandite solubility curve and from the zero point on the y-axis at the given
Chapter 6 Pozzolanic reactivity assessment

concentration of OH\(^-\). Technically, the theoretical saturated concentrations of CaO at those given x values (concentration of OH\(^-\)) at 40 °C need to be worked out first. This can be realised by using the formula given in BS EN 196-5, which is as follows:

\[
Y = \frac{350}{X - 15}
\]  

(1)

where X refers to the concentration of OH\(^-\) and Y refers to the theoretical saturated concentration of CaO at 40 °C. For each sample, the calculated concentration, Y, is subsequently compared with the actual CaO concentration measured by titration, and the difference in value refers to the CaO consumption, being presented as a percentage of the theoretical saturated concentration.

The quantified Frattini test results are all given below in Table 6.1. The negative percentages in the fixed CaO column are calculated from the data points which lie above the portlandite solubility curve. They should be normalised to 0% equivalent CaO consumption when they are correlated to the results of other pozzolanic reactivity testing methods.

Table 6.1 shows that more CaO was fixed on the 15-day for all the samples with positive percentages, which clearly indicates the continuing occurrence of pozzolanic reaction from 8-day to 15-day. The highest CaO fixation percentage, 39.4%, is found for PFA on the 15-day, while the highest within calcined London clay samples, 24.0%, is found for the one calcined at 900 °C on the 15-day.
# Table 6.1 Quantified Frattini test results

<table>
<thead>
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<th>Sample</th>
<th>Days</th>
<th>[OH\textsuperscript{-}] (mmol/l)</th>
<th>[CaO] (mmol/l)</th>
<th>T. S. [OH\textsuperscript{-}] (mmol/l)</th>
<th>Fixed [CaO] (%)</th>
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</thead>
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<td>8</td>
<td>60.2</td>
<td>9.7</td>
<td>7.7</td>
<td>-24.9</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>59.0</td>
<td>9.0</td>
<td>8.0</td>
<td>-12.6</td>
</tr>
<tr>
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</tr>
<tr>
<td></td>
<td>15</td>
<td>58.7</td>
<td>8.6</td>
<td>8.0</td>
<td>-7.2</td>
</tr>
<tr>
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<td>7.9</td>
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</tr>
<tr>
<td></td>
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<td>7.2</td>
<td>7.8</td>
<td>7.3</td>
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<td>15</td>
<td>60.8</td>
<td>6.2</td>
<td>7.6</td>
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<tr>
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</tr>
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<td></td>
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<td>61.3</td>
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<td>7.6</td>
<td>39.4</td>
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<td>7.5</td>
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</tr>
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<td>9.2</td>
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<td>7.5</td>
<td>11.0</td>
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<td>Ground sand</td>
<td>8</td>
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<tr>
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<td>15</td>
<td>61.8</td>
<td>9.2</td>
<td>7.5</td>
<td>-22.8</td>
</tr>
</tbody>
</table>

- CLC = calcined London clay, T. S. = theoretical saturated
6.2 Strength Activity Index (SAI) test

The strength activity index (SAI) test is an indirect method to assess the pozzolanic reactivity of materials. In this study, it was performed following the procedures specified in BS 3892 and BS EN 450-1. It involves compressive strength measurements over a period of curing time on the 50×50×50 mortar cubes, prepared according to the mix proportions shown in Table 4.2, and comparisons between control mortar and each of test mortar in terms of measured strengths.

Figure 6.3 is given below for a general overview on the compressive strength development of mortars over a whole curing period of 180 days.

![Figure 6.3 The compressive strength development of mortars over 180 days](image)

It is manifest in Figure 6.3 that the control mortar leads in the strength competition at the very early ages but GGBS mortar catches up with and overtakes it later on. At the late ages of this test, the two mortars containing clays calcined at 900 and 950 °C take over the leading position. In contrast, the mortar incorporating ground silica sand as cement replacement exhibits the lowest compressive strengths in most of time, which
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is not surprising to researchers. For a better and clearer illustration of the compressive strength development of mortars at different ages, the whole curing period of 180 days is divided into 5 parts, which are shown in Figure 6.4 a), b), c), d) and e), respectively.

a) 3 ~ 7 days

b) 7 ~ 14 days
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c) 14 ~ 28 days

![Graph showing compressive strength over curing time for different materials and temperatures.]

- Control
- 700°C calcined clay
- 850°C calcined clay
- 950°C calcined clay
- 1000°C calcined clay
- 600°C calcined clay
- 800°C calcined clay
- 900°C calcined clay
- 950°C calcined clay
- 1000°C calcined clay
- PFA
- GGBS
- Silica fume
- Sand

Compressive strength [MPa]
Curing time [Day]

---

d) 28 ~ 90 days

![Graph showing compressive strength over curing time for different materials and temperatures.]

- Control
- 600°C calcined clay
- 700°C calcined clay
- 800°C calcined clay
- 850°C calcined clay
- 900°C calcined clay
- 950°C calcined clay
- 1000°C calcined clay
- PFA
- GGBS
- Silica fume
- Sand

Compressive strength [MPa]
Curing time [Day]
e) 90 ~ 180 days

![Graph showing the compressive strength development of mortars at different ages: a) 3~7 days, b) 7~14 days, c) 14~28 days, d) 28~90 days, e) 90~180 days.]

Figure 6.4  The compressive strength development of mortars at different ages: a) 3~7 days, b) 7~14 days, c) 14~28 days, d) 28~90 days, e) 90~180 days

As shown in Figure 6.4 a), at the very early ages (3 and 7-day), the control mortar exhibits the higher compressive strength than any other studied mortar, which can be attributed to the previously mentioned dilution effect. The GGBS mortar follows the control mortar, taking the second position in this competition. It is interesting to note that the mortar containing ground silica sand shows a higher compressive strength than some mortars containing calcined clays on the third day. However, it was soon surpassed by some of those on the 7-day, and for the rest which are still inferior to it on the 7-day, the margin is considerably weakened. On the 14-day, it becomes to trail all the other mortars, as shown in Figure 6.4 b). At the same age, the GGBS mortar takes the leading from the control mortar, which is followed by silica fume, 900 °C, 850 °C and 950 °C calcined clay mortars. It can be observed in Figure 6.4 c) that silica fume mortar surpasses the control one on the 28-day, but still following the GGBS mortar. In addition, the mortar incorporating 900 °C calcined clay sample approaches the control mortar, leaving only a marginal difference in terms of compressive strength. In Figure 6.4 d), it is shown that more mortars gain higher strengths than the control
mortar on the 90-day, and there are only three mortars (ground silica sand, 600 and 700 °C calcined clays) interior to the control one in compressive strength on the 90-day. Favourably, the mortars containing calcined London clay (900 and 950 °C) claim the highest strengths at this age, surpassing the GGBS mortar. On the 180-day (Figure 6.4 e)), nothing changes noticeably in terms of strength development but the PFA mortar overtakes the 850 °C calcined clay mortar while the mortar containing 1000 °C calcined clay overwhelms that containing 800 °C calcined clay. The 600 and 700 °C calcined clay mortars, after 28 days, show higher strengths than the ground silica sand mortar only.

SAI test results are presented as percentages of the strength of control mortar at each specific curing age. They are given in Figure 6.5, where the strengths of control mortar at various times are all equivalent to the dash line at 1.0.

Due to the dilution effect induced by the 20 w.t% replacement of cement, no mortar compares favourably with the control mortar on the 3 and 7-day, with the SAI of most samples being less than 0.8. GGBS mortar becomes to exceed an SAI of 1.0 as early as on the 14-day, and the mortar containing silica fume manages to achieve that after
28 days. None of the calcined clay mortar samples gains a SAI equivalent to or higher than 1.0 on the 14 and 28-day. At the late ages (90 and 180-day), all the reported SAI values appear to be above 1.0, except those representing 600 and 700 °C calcined clays and ground silica sand. The mortars containing clays calcined at 900 and 950 °C gain the highest SAI values, overtaking the GGBS mortar which takes the leading at all early ages. Interestingly, there seem to be a momentum starting from the 14-day that 850, 900 and 950 °C are more effective than the other studied calcining temperatures in terms of allowing calcined clay mortars to gain a strength that is comparable to or higher than the control mortar. Moreover, among 600, 700 and 800 °C, higher temperature results in higher effectiveness, while a drop in the effectiveness can be seen from 950 to 1000 °C. At late ages, 900 and 950 °C appear to be the most effective temperatures with only marginal SAI differences in between, as shown in Figure 6.5. The silica sand mortar samples show a SAI of lower than 0.8 at all ages, due to the constant dilution effect and the pozzolanic inertness of sand.

It is stated in ASTM C618 that a test material can be considered as pozzolanic if the 28-day SAI is higher than 0.75 at the cement replacement level of 20%. In BS EN 450-1, the criterion for a test material being considered as pozzolanic is the 28-day and 90-day SAI must be greater than 0.75 and 0.85, respectively, at the replacement level of 20%. It is obvious in Figure 6.5 that all the studied materials, except ground silica sand, meet the above SAI requirements on the due days. This indicates the clays calcined at all the studied temperatures can be considered pozzolanic.
6.3 Portlandite consumption test

Portlandite consumption test is designed to directly evaluate the pozzolanic reactivity of materials. As cement is not involved in the portlandite consumption test, a fixed amount of commercial Ca(OH)$_2$ was used to react with test materials over a period of 90 days. For each mix, the amount of consumed Ca(OH)$_2$ can be calculated by subtracting the amount of remaining Ca(OH)$_2$ from the fixed starting amount. TGA technique was employed to quantify the remaining Ca(OH)$_2$ in each mix at different curing ages. The typical TGA data of portlandite-test material mixes cured for 28 days is given in Figure 6.6, as the development of weight loss with the increasing temperature.

![TGA data of portlandite-test material mixes after 28-day curing](image)

**Figure 6.6** TGA data of portlandite-test material mixes after 28-day curing

In Figure 6.6, all the portlandite-test material mixes exhibit two distinct weight loss phases (I and II). Phase I, which appears from ~400 to ~500 °C, can be attributed to dehydroxylation of portlandite, while phase II (roughly from 600 to 800 °C) is recognised as the consequence of decarbonation of CaCO$_3$. The mixes are meant to
vary in the weight loss during phase I, primarily depending on the pozzolanic reactivity of test materials. It is obvious in Figure 6.6 that the mixes incorporating calcined clay samples, PFA and silica fume are considerably higher than the mix containing silica sand in terms of the weight loss happening in phase I. Also it is interesting to note that for the mix containing GGBS, the weight loss in phase I is much more significant, as compared to the other SCM mixes. The weight reduction in phase II results from the decomposition of CaCO$_3$, which is formed by the inevitable carbonation of portlandite during the mixes preparation process. Furthermore, it should be noted that, prior to the noticeable phase I (<400 °C), there is a significant weight loss observed across all the mixes except the mix containing silica sand. This is believed to be associated with the dehydroxylation of pozzolanic reaction products, such as C-S-H, C-A-H and C-A-S-H phases. The absence of this weight loss, together with the observation of a more significant phase I weight loss, can suggest that silica sand does not possess pozzolanic reactivity. However, on the contrary, all the other test materials do so.

The results of portlandite consumption over a curing period of 90 days are expressed as Ca(OH)$_2$ in gram consumed by per gram of test material and presented in Figure 6.7.
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Figure 6.7 Portlandite consumption of all the mixes at various curing ages (3, 7, 14, 28 and 90-day)

It is unsurprising that the mix containing silica sand exhibits substantially less portlandite consumption than any other mix at all ages. The mixes incorporating calcined clay samples all display significant portlandite consumption at the very early age, and afterwards their portlandite consumption grew steadily with curing age up to 28 days. However, the increases in portlandite consumption for most of those mixes became minor from 28 to 90-day. There is a noticeable difference in the amount of portlandite consumed after 90 days amongst calcined clay mixes. The clay calcined at 900 °C shows the highest portlandite-fixing capacity (0.71 g/g), closely followed by the other calcined at 800 °C and higher (a capacity of ~0.70 g/g). In contrast, 600 and 700 °C calcined clays both show a capacity of around 0.60 g/g only. The mix containing PFA had a fairly slow start in portlandite consumption, exhibiting only a minor advantage over the mix containing silica sand on the 3-day, but it thereafter went through a rapid development of portlandite consumption, achieving a high 90-day value (0.78 g/g) that only the counterpart of silica fume mix is comparable to. Silica
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fume exhibits a high pozzolanic reactivity, as the mix shows highest portlandite consumptions at almost all ages. For the mix containing GGBS, the portlandite consumption was relatively stable throughout the whole curing period of 90 days. At all the ages later than 7-day, it was superior to the portlandite consumption of silica sand mix only.
6.4 Chapelle test

The Chapelle test is another direct method to assess the pozzolanic reactivity of pozzolans, and in literatures, it is very commonly used for testing metakaolin (Ferraz et al, 2015; Quarcioni et al, 2015). In this study, it allowed each test material to react with portlandite within an abundance of water at an elevated temperature (85 ± 5 °C) for a fixed length of time (16 hours). With similarities to Frattini test, chemical titration was used to determine the amount of the fixed Ca(OH)$_2$. The results are presented as the amount of Ca(OH)$_2$ in mg fixed by per gram of pozzolan, and they are all illustrated in Figure 6.8.

![Figure 6.8 Chapelle test results for calcined clays and other SCMs (0 mg/g for ground silica sand) (0 mg/g for ground silica sand)](image)

As can be seen from Figure 6.8, all the calcined clay samples exhibit a portlandite-fixing capacity of 400–600 mg/g, with the maximum (551.0 mg/g) being achieved at 900 °C. There is a clear trend among the clays calcined at 600, 700, 800 and 850 °C that the capacity increases gradually with the rising temperature. Furthermore, a steady decline in the capacity can be observed when the calcining temperature was raised from 900 to 950 °C as well as from 950 to 1000 °C. It is also interesting that the
other test materials vary greatly in the results of Chapelle test. PFA and GGBS both show portlandite fixation capacities less than half of any calcined clay sample, while silica fume displays an exceptionally high portlandite-fixing capability, being 1367.3 mg/g, two times higher than that of 900 °C calcined clay. Moreover, silica sand shows a capacity almost equivalent to zero.
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6.5 Discussion

One indirect (SAI test) and three direct methods (Frattini test, portlandite consumption test and Chapelle test) were carried out to assess the pozzolanic reactivity of clay samples activated at different calcining temperatures. PFA, GGBS, silica fume and ground silica sand were also examined with the four methods, providing comparisons with calcined clays in terms of their pozzolanic reactivity. Results have been given and depicted in Section 6.1, 6.2, 6.3 and 6.4. All the used calcining temperatures will be discussed in this section, in terms of the effect on activating the pozzolanic reactivity of London clay, which is aimed at finding out the optimum calcining temperature from them.

The results of XRD and FTIR analysis indicate that kaolinite can lose all the hydroxyl groups in the octahedral layers when calcined at 600 and 700 °C, completely transforming into metakaolin phase. However, illite and montmorillonite can retain most of their original crystallinity after calcination at such temperatures. In Figure 6.1 and 6.2, the clay samples calcined at 600 and 700 °C are observed lying above the portlandite solubility curve with the silica sand, suggesting that they can be labelled as non-pozzolanic in the Frattini test. Nonetheless, their SAI test results are 0.83 and 0.87 on the 28-day, and 0.88 and 0.91 on the 90-day, respectively. They are numerically greater than the threshold values stated in ASTM C618 and BS EN 450-1 for a material being conceived as pozzolanic. Furthermore, since silica sand is unable to react with portlandite, it is reasonable to use the mortar made with ground silica sand as a reference, whose strength development is irrelevant to pozzolanic reaction but inevitably dependent on dilution effect. In Figure 6.4 and 6.5, 600 and 700 °C calcined clays are considerably higher than silica sand at relatively late ages in terms of mortar strengths and SAI, which would not happen if 600 and 700 °C calcined clays were as inert as silica sand. In addition, it is well understood that the effect of pozzolanic reaction on the strength development of mortars usually become manifest at late ages. It is therefore reasonable to suggest that the clay samples calcined at 600 and 700 °C do possess pozzolanic reactivity. If silica sand remains used as a baseline for zero pozzolanic reactivity in the portlandite consumption test and Chapelle test, it can be seen in Figure 6.7 and 6.8 that clays calcined at 600 and 700 °C display portlandite-fixing capacity considerably higher than the baseline at all
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ages. Interestingly, there is a disagreement between Frattini test and all the other three tests, in terms of whether or not 600 and 700 °C calcined clays are considered pozzolanic. According to the XRD and FTIR data, the mineralogical compositions of the two calcined clays can include metakaolin, illite, montmorillonite and impurities. As pure metakaolin phase is acknowledged highly pozzolanic, it should be responsible for the ‘better than baselines’ results in the three tests. On the other hand, it is reported that quartz, as a filler, is capable of, by filler effect, stimulating cement hydration and causing more portlandite to form (Rahhal & Talero, 2008). The filler effect mechanism applies to all kinds of cement replacement materials with a particle fineness smaller than that of cement, and is irrelevant to pozzolanic reactivity. It is therefore possible that all the test materials had driven additional portlandite to be formed in the Frattini test samples. The clays calcined at 600 and 700 °C might not be able to consume all the additional portlandite but the other calcined clays managed to do, due to higher degrees of dehydroxylation and higher amorphous phase content. In addition, the Frattini test results of 600 and 700 °C calcined clays may possibly reflect that kaolinite is a minor constituent, as compared to the 2:1 clay minerals, in the mineralogical compositions of as-received London clay. It should also be mentioned that, when comparing 600 °C with 700 °C, higher degree of dehydroxylation may well explain why the clay calcined at the latter temperature was determined to be more pozzolanic.

Substantial improvement in pozzolanic reactivity testing is observed on the clay samples calcined at 800 and 850 °C. In particular, the duo was determined to settle in below the portlandite solubility curve on both testing ages in Frattini test. It is consistently agreed by all the testings that 800 and 850 °C are effective in activating the pozzolanic reactivity from London clay, and the latter temperature is modestly better than the former. Previous findings in the chapter of sample characterization reveal that the minimum studied temperature, which allows all hydroxyl groups to leave octahedral sheets of illite and montmorillonite, is 800 °C, but that is still not adequately high to cause significant damage to the layered 2:1 structures. A set of evidences, such as diminishing of characteristic X-ray reflections and shrinkage of the Si-O-Al bending peak, suggest that 850 °C is capable of delivering devastating structural change to those 2:1 clay minerals. Hence it can be readily understood that 800 and 850 °C compare favourably with 600 and 700 °C, due to the massive existence of 2:1 clay minerals.
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For the clays calcined at 900, 950 and 1000 °C, the results of pozzolanic reactivity tests are no longer positively correlated to calcining temperature, though they are still mostly superior to clays calcined below 900 °C. Specifically, 900 °C calcined London clay shows the highest pozzolanic activity across all the tests, with the only exception of 180-day SAI being marginally lower than that of 950 °C calcined clay. In addition, 1000 °C was determined to be less effective than either of the other two, and hence, discussion will be primarily focused on 900 and 950 °C. FTIR data shows that no vibration absorption peak associated with 2:1 clay minerals managed to make a survival under calcining at 900, 950 and 1000 °C. On the diffractogram, the reflections from illite and montmorillonite are extremely weak at 900 °C, and become completely invisible at 950 and 1000 °C. Both findings could demonstrate the completion of amorphization for illite and montmorillonite at the three specific temperatures. This well explains the reason why 900, 950 and 1000 °C are superior to 600, 700, 800 and 850 °C in terms of activating pozzolanic reactivity of London clay. On the other hand, as discussed previously, XRD data shows that calcining at 950 and 1000 °C can lead to recrystallization of spinel, which has adverse effect on the amorphization of clay minerals and, accordingly, should be avoided. There is obviously a trade-off existing in the calcining process between transforming as much crystalline phase into amorphous phase as possible and preventing the occurrence of recrystallization. It is clear from XRD analysis that the calcining temperature range 900–950 °C is most sensitive to the trade-off, and therefore, it is reasonable to assume that the optimum calcining temperature should be either 900 °C or 950 °C. As stated earlier, the overall result of pozzolanic reactivity assessments shows that the clay calcined at 900 °C is more reactive than any other calcined clay.

There are some other interesting findings obtained from the analysis of pozzolanicity assessment results. As shown in Table 5.6, BET surface area decreases with the increase of calcining temperature. The results of pozzolanic reactivity assessment show that the decrease in specific surface area did not appear to be a limitation on the pozzolanic reactivity, which is contrary to the findings of Alujas et al (2015). In the portlandite consumption test, it is observed that the amount of portlandite fixed by the most pozzolanic sample (900 °C calcined clay) became a relatively constant value after 28 days. Since all mixes contained excess portlandite, it is reasonable to suppose that almost all the reactive phase within 900 °C calcined clay should have been
involved in reacting with portlandite by the 90-day. For 900 °C, the amount of consumed portlandite on the 90-day was ~0.71 g/g of calcined London clay. It was suggested in literatures that 1g of metakaolin or calcined montmorillonite can consume ~1 g of portlandite by the end of a complete pozzolanic reaction (Murat, 1983; He et al, 1994). It can therefore be estimated that 900 °C calcined London clay comprises ~30 wt.% non-pozzolanic phase. Calcined illite phase could be included in the ~30 wt.% because it has very low reactivity and cannot be considered pozzolanic (He et al, 1995; He et al, 2000; Fernandez et al, 2011). Furthermore, if all of these are considered jointly with the estimated percentages of kaolinite (~30.2 wt.%), illite/montmorillonite (~53.2 wt.%) and impurities (~16.6 wt.%) in as-received London clay, as stated in Section 5.7, the individual percentage of illite in as-received London clay can be worked out as 11.9 wt.%, and accordingly, the rest 41.3 wt.% is for montmorillonite. As a result, the mineralogical compositions of London clay can be quantitatively expressed in Table 6.2. However, the same assumptions adopted in Section 5.7 apply here as: nothing other than kaolinite, illite and montmorillonite is contributory to the weight loss within the range 350~950 °C; there is no overlap in dehydroxylation temperatures. It is worth emphasizing that the ‘impurities’ in this calculation refer to all accompanying minerals that are considered non-pozzolanic, such as pyrite, feldspar and quartz.

**Table 6.2** Estimated mineralogical compositions of London clay

<table>
<thead>
<tr>
<th>Minerals</th>
<th>Percentages (wt.%)</th>
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</thead>
<tbody>
<tr>
<td>Kaolinite</td>
<td>~30.2</td>
</tr>
<tr>
<td>Illite</td>
<td>~11.9</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>~41.3</td>
</tr>
<tr>
<td>Impurities</td>
<td>~16.6</td>
</tr>
</tbody>
</table>

work, they were joined by ground silica sand to draw comparisons with various calcined clays. The results prove that all the employed testing methods were technically valid, and also suggest that London clay calcined at the optimum temperature is comparable to them in the ability of fixing portlandite and providing mortars with enhanced strengths. Interestingly, unlike PFA and silica fume, GGBS seems to be inconsistent in the results of pozzolanic reactivity assessment. It is located above the portlandite solubility curve on both testing ages in Frattini test, implying ‘non-pozzolanic’ character, and it consumed less amount of portlandite than any other test material except silica sand after 14 days, as shown in Figure 6.7. In contrast, the mortar with 20 wt.% GGBS content exhibited highest strengths until the age of 28-day, after which it was modestly overtaken by the competitors incorporating clays calcined at 900 and 950 °C but still superior to the other and control. GGBS is widely considered as a latent hydraulic material rather than pozzolanic because it will hydrate upon contact with water. However, the dissolution of Si, Al, Ca and Mg, which are the most typical and dominant elements of GGBS, is highly pH-dependent. When the system pH is below 11.5, the solubility of silica appears to be very low whereas Ca and Mg tend to be dissolved into the solution. Consequently, this would lead to the formation of a thin and impermeable aluminosilicate layer on the surface of the GGBS grains, which impedes any further hydration (Song & Jennings, 1999; Konsta-Gdoutos & Shah, 2003). Alkaline activator, such as portlandite or sodium hydroxide, is usually required to prevent the formation of the impermeable layer by elevating the pH to higher than 11.5, facilitating further hydration of GGBS grains (Thomas, 2013). This is also the way how portlandite is consumed in a cement-GGBS blended system, attacking and disintegrating the formed aluminosilica layer at a pH > 11.5. Therefore the dissolution rate of GGBS depends largely on the alkali concentration of the reacting system (Wang & Scrivener, 1995). This can explain the reason why GGBS failed to qualify for the pozzolanic area in Frattini test. There could be a competition for available water between GGBS and Portland cement once water is added into the dry sample mix. Due to the very much water addition, making a w/b ratio of 5, the concentration of portlandite generated from cement hydration was significantly reduced, as compared to that of a regular cement paste, mortar or concrete system with a w/b ratio of 0.3, 0.4 or 0.5. As a result, the pH might be too low to allow the hydration of aluminosilicate layer-covered GGBS grains to advance. Moreover, filler effect should also work in this case, stimulating the hydration of Portland cement.
Hence it can be concluded that a combination of these effects decided the result of Frattini test for GGBS. In the portlandite consumption test, the majority of added water might have been used to dissolve portlandite, reacted with GGBS and allow dissolved portlandite to be consumed in disintegrating the unfavourable grain cover during the first 3 days. The remaining water content was possibly insufficient to cause more portlandite consumption later on, leaving relatively constant value, as shown in Figure 6.7.

The correlations between the SAI test and the other tests are presented in Figure 6.9, 6.10 and 6.11. For each test, the results at relatively late ages are selected to draw the correlations, as they can best represent the outcome of pozzolanic reaction. It is clear that there are considerable correlations between the 90-day SAI results and the late age results of other tests.

![Figure 6.9 Correlation between measured pozzolanic reactivity of calcined London clays using the SAI test (90-day) and the Frattini test (15-day)](image-url)
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Figure 6.10 Correlation between measured pozzolanic reactivity of calcined London clays using the SAI test (90-day) and the portlandite consumption test (90-day)

Figure 6.11 Correlation between measured pozzolanic reactivity of calcined London clays using the SAI test (90-day) and the Chapelle test
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In conclusion, the results of pozzolanic reactivity assessments show that 900 °C is most effective from all the studied calcining temperatures in thermally activating the pozzolanicity potential of London clay. Moreover, the clay calcined at 900 °C exhibited comparable pozzolanicity to PFA, GGBS and silica fume. It can therefore be readily understood that the clay calcined at this optimum temperature was selected for the subsequent concrete testing experiments.
Chapter 7 PERFORMANCE OF CONCRETE CONTAINING CALCINED LONDON CLAY
7.1 Calcined clay lump

The calcination of raw clay lumps was conducted at 900 °C, as this was by far determined to be the optimum temperature in activating the pozzolanic reactivity of London clay. The calcined product lumps appeared to have a relatively thin light brown/red surface layer, whereas the bulk of the spherical body formed a black core, as shown in Figure 4.3 b) and c). The distinction in colour is very often seen on fired clay ceramics, and is believed to be due to the difference in the oxidation state of iron across the lump sample (MacKenzie & Cardile, 1990). As suggested by elemental analysis in Table 5.1, Fe accounts for about 7.66 wt.% of as-received London clay. Iron-bearing minerals (e.g. goethite) can be easily transformed into hematite (α-Fe₂O₃) upon a 2-hour-long calcining at 900 °C. It is therefore reasonable to suppose that the light brown/red colour on the outer rim of calcined lumps results from the formation of hematite. In contrast, due to the spherical geometry, the core and most interior area of raw clay lumps was prevented from having sufficient contact with oxygen in the air, leaving ferrous minerals in that area un-oxidized. There might be another reason that is possibly responsible for the black colour. In the interior area, the lack of oxygen could lead to the insufficient oxidation of carbonaceous material, which might generate the reducing gas CO (Brownell, 1957). Since the formed CO can hardly escape from the inside of a lump, it could create a local reducing environment for iron-bearing minerals. Dark coloured magnetite (Fe₃O₄) was formed as a result of a series of possible reducing reactions. The ground calcined clay lumps appeared to be a dark brown powder as shown in Figure 4.3 d).

The black core was examined using XRD, and the data is shown in Figure 7.1, which also includes the diffractogram of 900 °C calcined clay. It is clear that the hematite reflections at 24.2, 33.3 and 35.7 °2θ, which can be observed for 900 °C calcined clay, are absent for the black core. The weak reflection that appears at about 43.8 °2θ can evidence the presence of magnetite in the black core. Both findings support the explanations on the distinction in colour.
Figure 7.1 Diffractogram for black core and 900 °C calcined clay
7.2 Fresh concrete

Prior to being cast into moulds, fresh concrete was examined for workability by slump test. The results are summarized in Table 7.1, and two examples of the tested slump were shown in Figure 7.2.

Table 7.1 Slump test results of all concrete mixes

<table>
<thead>
<tr>
<th>Concrete mixes</th>
<th>Slump (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-0.5-000</td>
<td>150</td>
</tr>
<tr>
<td>C-0.5-10C</td>
<td>160</td>
</tr>
<tr>
<td>C-0.5-20C</td>
<td>155</td>
</tr>
<tr>
<td>C-0.5-30C</td>
<td>140</td>
</tr>
<tr>
<td>C-0.4-000</td>
<td>60</td>
</tr>
<tr>
<td>C-0.4-10C</td>
<td>85</td>
</tr>
<tr>
<td>C-0.4-20C</td>
<td>45</td>
</tr>
<tr>
<td>C-0.4-30C</td>
<td>60</td>
</tr>
<tr>
<td>C-0.3-000</td>
<td>0</td>
</tr>
<tr>
<td>C-0.3-10C</td>
<td>0</td>
</tr>
<tr>
<td>C-0.3-20C</td>
<td>0</td>
</tr>
<tr>
<td>C-0.3-30C</td>
<td>0</td>
</tr>
<tr>
<td>C-0.4-20P</td>
<td>90</td>
</tr>
<tr>
<td>C-0.4-20S</td>
<td>0</td>
</tr>
<tr>
<td>C-0.4-20G</td>
<td>80</td>
</tr>
</tbody>
</table>

It is obvious in Table 7.1 that for the concrete mixes containing calcined London clay, lower w/b ratios resulted in worse workability. Particularly, zero results were obtained at a w/b ratio of 0.3, regardless of the SCM replacement level. Significantly workable
concrete can be achieved by lifting the w/b ratio to 0.5. Figure 7.3 illustrates how the results of slump test change with the increasing calcined clay replacement levels (10, 20, 30 wt.%).

**Figure 7.3** Slump test results of concrete mixes incorporating 10, 20 and 30 wt.% calcined London clay at 0.3, 0.4 and 0.5 w/b ratios

For the w/b ratio of 0.5, as shown in Figure 7.3, the workability had not changed significantly across three different replacement levels. When the w/b ratio was 0.4, improvement in workability can be observed at 10 wt.% replacement level. 20 wt.% replacement compared unfavourably with 0 wt.% replacement, in terms of the height of slumps. At 30 wt.%, the slump was measured to be equivalent to the control mix. For the mixes with a w/b ratio of 0.3, results were consistently zero, and seemed to be irrelevant to replacement levels.

The slump test results of concretes containing 20 wt.% different SCMs with an identical w/b ratio of 0.4 are given in Figure 7.4.
As expected, due to the spherical shape of particles, a substitution of 20 wt.% PFA noticeably improved the workability of concrete. The slump of concrete containing GGBS was also higher than that of the control concrete. In contrast, the concrete containing silica fume was measured to have a zero slump test result, which is because agglomerates of silica fume trapped some water, leaving inadequate water to provide lubrication to the whole mixture.

**Figure 7.4** Slump test results of concretes incorporating various SCMs with a w/b ratio of 0.4 (0 mm for 20wt.% SF)
7.3 Hardened concrete

7.3.1 The colour of concretes

Due to the relatively high iron content, the colour issue might in the future become a major concern for the application of calcined London clay in concrete. For the architectural and marketing purposes, it would be crucial to ensure that the concrete incorporating calcined London clay is visually similar to the conventional concrete. As emphasized before, calcining in the form of lumps was especially aimed at addressing the colour issue. Figure 7.5 presents the appearances of concrete cubes made with various w/b ratios (0.3, 0.4 and 0.5) and various cement replacement levels (0, 10, 20 and 30 wt.%).

![Concrete cubes containing calcined London clay made with w/b ratios of a) 0.5, b) 0.4 and c) 0.3 at various replacement levels (from left to right: 0, 10, 20 and 30 wt.%), and d) concrete cubes made with a 0.4 w/b ratio and 20 wt.% replacement level (from left to right: control, calcined London clay, PFA, silica fume and GGBS)](image)

As shown in Figure 7.5 a), b) and c), for the concretes with a specific replacement level of calcined London clay, there seemed to be no variation in colour at all between 0.3, 0.4 and 0.5 w/b ratios. Interestingly, it is also found that at any of the studied w/b ratios, the colour of cubes became increasingly dark with the rise in replacement level. Overall, the colour change of concretes induced by the addition of calcined London clay...
clay appeared to be insignificant. In Figure 7.5 d), the addition of other SCMs also caused slight colour changes to concrete cubes. The cube containing silica fume is considerably darker than any of the others, whilst calcined London clay and PFA appeared to have the least effect on concrete colour.

### 7.3.2 Concrete densities

Concrete densities were measured, and each reported value in Table 7.2 is an average for 15 cubes over all ages (3, 7, 14, 28 and 90 days). Theoretical densities, which were calculated from concrete mix proportions, are also reported in Table 7.2.

**Table 7.2 Measured and theoretical densities of concretes**

<table>
<thead>
<tr>
<th>Concrete mixes</th>
<th>Measured density (kg/m³)</th>
<th>Theoretical density (kg/m³)</th>
<th>Difference (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-0.5-000</td>
<td>2330</td>
<td>2267</td>
<td>2.7</td>
</tr>
<tr>
<td>C-0.5-10C</td>
<td>2318</td>
<td>2264</td>
<td>2.3</td>
</tr>
<tr>
<td>C-0.5-20C</td>
<td>2313</td>
<td>2260</td>
<td>2.3</td>
</tr>
<tr>
<td>C-0.5-30C</td>
<td>2301</td>
<td>2257</td>
<td>1.9</td>
</tr>
<tr>
<td>C-0.4-000</td>
<td>2354</td>
<td>2303</td>
<td>1.5</td>
</tr>
<tr>
<td>C-0.4-10C</td>
<td>2338</td>
<td>2303</td>
<td>1.5</td>
</tr>
<tr>
<td>C-0.4-20C</td>
<td>2332</td>
<td>2300</td>
<td>1.4</td>
</tr>
<tr>
<td>C-0.4-30C</td>
<td>2326</td>
<td>2296</td>
<td>1.3</td>
</tr>
<tr>
<td>C-0.3-000</td>
<td>2377</td>
<td>2359</td>
<td>0.7</td>
</tr>
<tr>
<td>C-0.3-10C</td>
<td>2367</td>
<td>2355</td>
<td>0.5</td>
</tr>
<tr>
<td>C-0.3-20C</td>
<td>2354</td>
<td>2351</td>
<td>0.1</td>
</tr>
<tr>
<td>C-0.3-30C</td>
<td>2336</td>
<td>2346</td>
<td>0.4</td>
</tr>
<tr>
<td>C-0.4-20P</td>
<td>2327</td>
<td>2284</td>
<td>1.9</td>
</tr>
<tr>
<td>C-0.4-20S</td>
<td>2279</td>
<td>2282</td>
<td>0.1</td>
</tr>
<tr>
<td>C-0.4-20G</td>
<td>2332</td>
<td>2305</td>
<td>1.1</td>
</tr>
</tbody>
</table>

It is manifest that the measured densities are significantly consistent with the calculated theoretical values. For a clearer illustration on how concrete densities were affected by w/b ratios and replacement levels, Figure 7.6 is given below.
Figure 7.6 Densities of concretes containing calcined London clay at different replacement levels (0.3, 0.4 and 0.5)

Figure 7.6 shows that, as expected, the higher the w/b ratio, the lower the concrete density. Moreover, for a given w/b ratio, the higher the replacement level, the lower the concrete density.

### 7.3.3 The strength development of concretes

The compressive strengths of concretes were measured and recorded on the 3, 7, 14, 28 and 90-day. Results are provided in Table 7.3, 7.4, 7.5 and 7.6, and plotted against curing age in Figure 7.7 a), b) and c) and Figure 7.8.
### Table 7.3 Compressive strengths of concretes containing calcined London clay with a w/b ratio of 0.5

<table>
<thead>
<tr>
<th>Concrete mixes</th>
<th>3-day MPa</th>
<th>7-day MPa</th>
<th>14-day MPa</th>
<th>28-day MPa</th>
<th>90-day MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-0.5-000</td>
<td>35.2</td>
<td>41.7</td>
<td>45.7</td>
<td>49.9</td>
<td>54.3</td>
</tr>
<tr>
<td>C-0.5-10C</td>
<td>30.1</td>
<td>37.4</td>
<td>41.7</td>
<td>47.8</td>
<td>51.6</td>
</tr>
<tr>
<td>C-0.5-20C</td>
<td>27.2</td>
<td>36.2</td>
<td>42.2</td>
<td>46.3</td>
<td>53.8</td>
</tr>
<tr>
<td>C-0.5-30C</td>
<td>24.2</td>
<td>31.2</td>
<td>37.4</td>
<td>43.1</td>
<td>49.9</td>
</tr>
</tbody>
</table>

### Table 7.4 Compressive strengths of concretes containing calcined London clay with a w/b ratio of 0.4

<table>
<thead>
<tr>
<th>Concrete mixes</th>
<th>3-day MPa</th>
<th>7-day MPa</th>
<th>14-day MPa</th>
<th>28-day MPa</th>
<th>90-day MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-0.4-000</td>
<td>42.3</td>
<td>48.5</td>
<td>54.0</td>
<td>56.4</td>
<td>59.8</td>
</tr>
<tr>
<td>C-0.4-10C</td>
<td>38.6</td>
<td>45.5</td>
<td>49.7</td>
<td>54.6</td>
<td>58.7</td>
</tr>
<tr>
<td>C-0.4-20C</td>
<td>36.9</td>
<td>44.7</td>
<td>50.7</td>
<td>58.0</td>
<td>63.0</td>
</tr>
<tr>
<td>C-0.4-30C</td>
<td>34.6</td>
<td>42.0</td>
<td>50.4</td>
<td>55.6</td>
<td>60.9</td>
</tr>
</tbody>
</table>

### Table 7.5 Compressive strengths of concretes containing calcined London clay with a w/b ratio of 0.3

<table>
<thead>
<tr>
<th>Concrete mixes</th>
<th>3-day MPa</th>
<th>7-day MPa</th>
<th>14-day MPa</th>
<th>28-day MPa</th>
<th>90-day MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-0.3-000</td>
<td>56.2</td>
<td>59.4</td>
<td>62.5</td>
<td>63.1</td>
<td>69.9</td>
</tr>
<tr>
<td>C-0.3-10C</td>
<td>56.0</td>
<td>59.5</td>
<td>64.6</td>
<td>67.3</td>
<td>75.6</td>
</tr>
<tr>
<td>C-0.3-20C</td>
<td>54.2</td>
<td>57.4</td>
<td>64.8</td>
<td>69.8</td>
<td>77.2</td>
</tr>
<tr>
<td>C-0.3-30C</td>
<td>48.1</td>
<td>59.6</td>
<td>62.7</td>
<td>67.2</td>
<td>74.2</td>
</tr>
</tbody>
</table>

### Table 7.6 Compressive strengths of concretes containing 20 wt.% various SCMs with a w/b ratio of 0.4

<table>
<thead>
<tr>
<th>Concrete mixes</th>
<th>3-day MPa</th>
<th>7-day MPa</th>
<th>14-day MPa</th>
<th>28-day MPa</th>
<th>90-day MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-0.4-20P</td>
<td>33.4</td>
<td>38.9</td>
<td>46.2</td>
<td>49.8</td>
<td>63.0</td>
</tr>
<tr>
<td>C-0.4-20S</td>
<td>37.6</td>
<td>46.5</td>
<td>51.9</td>
<td>57.8</td>
<td>61.5</td>
</tr>
<tr>
<td>C-0.4-20G</td>
<td>36.7</td>
<td>45.1</td>
<td>50.5</td>
<td>55.5</td>
<td>62.3</td>
</tr>
</tbody>
</table>
Chapter 7 Performance of concrete containing calcined London clay

a) \( w/b = 0.5 \)

b) \( w/b = 0.4 \)
As expected, for a given replacement level, samples with a w/b ratio of 0.3 exhibited the greatest compressive strengths at all ages, followed by 0.4 and 0.5. On the 3-day, all samples incorporating calcined London clay showed lower strengths than the control samples. The loss in strength at early age was primarily due to the dilution effect, and it appeared to be more pronounced with higher w/b ratio as well as higher cement replacement level. Additionally, samples with a higher w/b ratio appeared to require more curing time to narrow and eliminate the initial strength discrepancies. The effect of pozzolanic reaction became noticeable from the 7-day, which is particularly based on the observation that the test samples with a w/b of 0.3 (C-0.3-10C and C-0.3-30C) gained strengths slightly higher than the control sample (C-0.3-000) on the 7-day. At the later ages, the control sample at 0.5 w/b had not been overtaken by any of the sample containing calcined London clay, although C-0.5-20C very nearly equalized it on the 90-day. In Figure 7.7 b), the 20 wt.% cement replacement by calcined London clay enabled the corresponding sample to have 28 and 90-day compressive strengths exceeding those of the control sample. The 0.4 w/b sample with 30 wt.% cement substituted by calcined London clay (C-0.4-30C) also showed

**Figure 7.7** Compressive strength development of concrete samples made with 0, 10, 20 and 30 wt.% calcined London clay at various w/b ratios: a) 0.5; b) 0.4; c) 0.3
superior strength to the control sample on the 90-day, but it was still lower than the former. The improvement in compressive strength owing to the addition of calcined London clay was most pronounced for the w/b ratio of 0.3, as shown in Figure 7.7 c). All those samples (C-0.3-10C, C-0.3-20C and C-0.3-30C) exhibited, from the 14-day onwards, greater strengths than the control. Again 20 wt.% appeared to be the optimum replacement level in this case, because it resulted in the highest strengths at late ages.

![Figure 7.8 Compressive strength development of concrete samples made with 20 wt.% various SCMs (calcined London clay, PFA, silica fume and GGBS) at the w/b ratio of 0.4](image)

Because of the dilution effect, no concrete samples gained comparable strengths to the control by the 14-day. The effect of pozzolanic reaction (hydraulic reaction for GGBS) appeared to be particularly significant on the 28-day, as both C-0.4-20C and C-0.4-20S overtook the control by clear margins at that age. Furthermore, all the concrete samples containing SCMs appeared to be higher than the control in terms of the 90-day compressive strength. To conclude the results of strength testing, calcined London clay is highly comparable to the other SCMs at the particular w/b ratio (0.4) and cement replacement level (20 wt.%).
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7.3.4 Efficiency factor

The concept of efficiency factor is adopted to further assess the relative performance of the studied SCMs in concrete. The efficiency factor $k$ is defined as:

$$ k = \frac{R_s m_{co} - m_c}{m_{SCM}} $$

where $R_s$ is the relative strength (strength of concrete incorporating a SCM divided by strength of control concrete at a same age), $m_{scm}$ is the SCM content (kg/m$^3$) in the blended mix, $m_{co}$ and $m_c$ are the cement content (kg/m$^3$) in the control and blended mix, respectively (Wong & Abdul Razak, 2005). If a $k$ factor equals to 1, it would mean that the SCM has the same cementing efficiency as Portland cement. In other words, this SCM can substitute Portland cement on a weight-to-weight basis and the strength of concrete does not change at all. Accordingly, a $k$ factor less than 1 would indicate a lower efficiency, while the value of $k$ would be expected to be greater than 1 for a higher efficiency. The results are all given in Figure 7.9 and 7.10.

a) $w/b = 0.5$

![Efficiency factor vs Curing time graph with different percentages of calcined London clay]

- 10 wt.% calcined London clay
- 20 wt.% calcined London clay
- 30 wt.% calcined London clay
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b) $w/b = 0.4$

![Graph showing strength efficiency factors for calcined London clay in concretes with different replacement levels at $w/b$ ratios: a) $w/b = 0.5$; b) $w/b = 0.4$; c) $w/b = 0.3$.](image)

Figure 7.9 Strength efficiency factors of calcined London clay in concretes with different replacement levels at $w/b$ ratios: a) $w/b = 0.5$; b) $w/b = 0.4$; c) $w/b = 0.3$
Figure 7.10 Strength efficiency factors of SCMs in concretes with a 20 wt.% replacement level and a w/b ratio of 0.4

As shown in Figure 7.9 a), b) and c), the efficiency factors appeared to be increasingly greater with curing time, which implies that the strength development of concretes containing calcined London clay was at a greater rate than that of control concretes at almost all ages. The highest $k$ value on the 90-day is found to be up to 1.8 for 10 wt.% replacement level under the w/b ratio of 0.3, followed by 20 and 30 wt.% replacement levels. Both of those were also higher than 1.0. By contrast, none of the concretes with a 0.5 w/b achieved a 90-day $k$ value exceeding 1.0. For the 0.4 w/b, the concrete with 10 wt.% Portland cement substituted failed to accomplish a $k$ (>1) value on the 90-day but the other two mixes (20 and 30 wt.% replacement) achieved that. The results presented in Figure 7.10 suggest the efficiency factor of calcined London clay is comparable to that of silica fume at all ages. PFA and GGBS experienced a relatively slow start in the development of efficiency factor but they managed to diminish the margin with calcined London clay and silica fume by the 90-day.
7.4 Discussion

7.4.1 Influence of calcined London clay and other SCMs on the workability of concrete

The workability of fresh concrete is largely dependent on the employed w/b ratios. It is widely acknowledged that the higher the w/b ratio, the better the workability of concrete. In the case of this study, it has been presented in Figure 7.3 that the w/b ratio of 0.5 resulted in the highest workability, followed by the w/b 0.4 and 0.3. This is because, with higher w/b ratio, there can be more free water available to serve as a lubricant between solid particles. At the 0.3 w/b, water should have mostly been used to form a water film layer on the surfaces of binder material particles and aggregates. Given that there was also some water trapped during cement particle flocculation, the remaining free water was therefore inadequate to introduce a lubrication effect into the fresh mix. As a result, a zero slump was recorded.

The adverse effect of replacing Portland cement with calcined clay (or metakaolin) on the workability of concrete has been spotted by a number of preceding researchers, such as Bai et al (1999), Sabir, Wild & Bai (2001), Qian & Li (2001), Brooks & Megat Johari (2001), Kim, Hwang & Lee (2012), Amankwah, Bediako & Kankam (2014) and Barbhuiya, Chow & Memon (2015). On the contrary, Rashad (2013) suggested in his work that the addition of metakaolin can improve the workability of concrete, as well as mechanical properties and durability. There have also been some researchers, suggesting that the degree of replacement can play an influential role. Ding & Li (2002) reported that the workability of concretes (w/b = 0.35) with 5 and 10 wt.% of Portland cement substituted by metakaolin was improved, as compared to the control concrete. However, a decrease in workability occurred with a 15 wt.% metakaolin replacement. Wu (2006) stated similar findings, but the decrease of workability (w/b = 0.3, with the addition of 3 wt.% super-plasticiser) was reported to happen when the replacement level was raised to 20 wt.%. For this study, it can be seen in Figure 7.3 that only the slump at the w/b ratios of 0.4 was relatively sensitive to the replacement level.

The improvement in workability at w/b 0.4 and 10 wt.% replacement level was possibly attributable to the ball-bearing effect. The particles of admixture material can act as ball-bearing to facilitate the water lubrication, and subsequently improve the fluidity of
concrete (Thomas, 2013). This effect is considered most pronounced for those admixture materials with particles in spherical shape. However, the particles of calcined London clay appear to be in irregular shape, as displayed in Figure 5.5. It is, therefore, still uncertain that the ball-bearing effect of calcined clay particles worked to what degree. Moreover, fine calcined clay particles can fill the void space in cement flocs, which is meant to be occupied by water in the absence of SCMs. As a result, the packing of binder particles was improved, and more water was available to act as lubricant and then contribute to the workability of concrete. This could be another factor leading to the improved workability at \( w/b \) 0.4 and 10 wt.% replacement level. The worsened concrete workability at \( w/b \) 0.4 and 20 wt.% replacement level may be due to the following reason. Since calcined clay particles were smaller in size than Portland cement, the increase of calcined clay content in concrete inevitably raised the total surface area of dry mix. More of the added water was used to wet the surfaces of particles, leaving less to provide lubrication to the whole mixture. It should be noted that the mentioned effects of partially replacing Portland cement with calcined London clay on the workability of concrete, no matter favourable or unfavourable, co-existed at all times. These slump test results could imply that the ball-bearing effect and the packing effect played more dominantly at lower replacement levels but they were overtaken by the last effect as the amount of calcined clay content increased, resulting in a decreased workability. It is interesting to note that the workability of concrete at \( w/b \) 0.4 and 30 wt.% replacement level was improved to be equivalent to that of the corresponding control concrete but it was still inferior to that at 10 wt.%.. It is still unclear why this happened, and it might be within the acceptable error range. A replacement level of 25 wt.% could be adopted to draw further comparisons with 20 and 30 wt.%.

At the \( w/b \) ratio of 0.3, slumps consistently equalled to zero. At the \( w/b \) ratio of 0.5, due to the sufficient availability of water as lubricant, all the previously discussed effects faded out. The workability of concrete mixes with a \( w/b \) ratio of 0.5, therefore, had not altered significantly across all the replacement levels.

As expected, the addition of 20 wt.% PFA greatly improved the workability of concrete with a \( w/b \) ratio of 0.4. This is due to the spherical shape of PFA particles, which are shown in Figure 5.6. The ball-bearing effect worked particularly well with spherical particles. Additionally, Nicolas, Cyr & Escadeillas (2014) reported that flash-calcined metakaolin contained about 10~15 wt.% spherical particles, and, as a consequence,
it compared favourably with the metakaolin produced from traditional calcination, in terms of the effect on improving the workability of concrete. GGBS consists of, primarily, small smooth slip planes, as can be seen in Figure 5.7. It appeared to be capable of improving the workability of concrete as well. Furthermore, Virgalitte et al (1995) suggested that GGBS has lower water demand, owing to the slower hydration than Portland cement, and hence more water is available for lubrication. It is unsurprising to observe a zero slump for the concrete containing silica fume. Densified silica fume lumps can only be partially broken down to fine particles during mechanical mixing (Diamond, Sahu & Thaulow, 2004). The agglomerates of silica fume can trap some of the mixing water, leading to inadequate water serving as lubricant in concrete (Kong et al., 2013).

7.4.2 The influence of w/b ratio and cement replacement level on the density of concrete

It is clear in Figure 7.6 that concretes with lower w/b ratio had higher densities. This is because, with lower w/b ratio, there was more Portland cement involved in making concrete. For a given volume, this concrete must be heavier than those with a higher w/b. Also it is consistent across all w/b ratios that concretes with higher amount of cement replaced by calcined London clay had lower densities. This can be simply attributed to the fact that calcined London clay has a density lower than Portland cement.

It is also interesting to see, from Figure 7.6, the changes in the difference between measured density and theoretical density when the w/b ratio rose from 0.3 to 0.5. At the w/b ratio of 0.5, the difference values were around or slightly higher than 2.0%, but those of w/b 0.4 mixes decreased to between 1.3 and 1.5%. Furthermore, the difference values of w/b 0.3 mixes all dropped to below 1.0%. In the concrete mix proportions design, the volume proportion of air content was consistently assumed to be 1.0%. During fresh concrete casting, although a vibration table was employed to help expel air bubbles entrapped in the mixture until there were no visible air bubbles emerging on the top surface of the mixture, there should be still some air surviving inside the mixture. The volume of survived air could be dependent on the workability of fresh concrete (i.e. the w/b ratio). The higher the w/b ratio, the less the volume of survived air. Since the mixing procedure was completely identical, this can be
confirmed by observing much more air bubbles emerging on the top surface of a higher w/b ratio mixture than a lower ratio mixture during casting. This may well explain the changes in density difference across the w/b ratios. At the w/b ratio of 0.5, the volume proportion of air content (i.e. survived air) could be less than the assumed value of 1.0%, leading to a relatively large difference between measured and theoretical densities. The volume proportion of air content at w/b 0.4 could be closer to 1.0% than that at w/b 0.5, and it is even more so at w/b 0.3. It is therefore reasonable to conclude that the closer to 1.0% the volume proportion of air content, the smaller the difference between measured density and theoretical density.

In addition, it is unsurprising that the density difference value of silica fume mixture was only 0.1%. This is because of the inferior workability of the mixture, which led to a reasonably large volume of air content during casting.

7.4.3 The influence of calcined London clay and other SCMs on the strength development of concrete

The effect of partially substituting Portland cement with calcined London clay on the strength development of concrete can be considered from different aspects. First of all, since a certain amount of calcined London clay was introduced to join a concrete mix as an alternative binder, Portland cement content was inevitably diluted in the mix. The dilution effect can cause concretes significant loss of early strength, depending on the specific amounts replaced. At a given w/b ratio, the greater the replaced amount was, the more the early strength loss was, which is clearly illustrated in Figure 7.7 a), b) and c). Secondly, the finely divided clay minerals, quartz and other impurities may fill up the capillary pores between cement particles, providing additional nucleation sites that allow the further growth of C-S-H gel released from cement hydration, which is the filler effect. Even though fillers appeared to accelerate the hydration of Portland cement and have contribution in refining the size of pores, the effect itself was still unable to fully compensate the loss in strength resulted from the dilution effect unless pozzolanic reaction participated. And this comes to the last aspect. The reactive components of calcined London clay, such as metakaolin and calcined montmorillonite, reacted with portlandite released from cement hydration to form a range of products. For instance, the pozzolanic reaction products of metakaolin can include C-S-H, C₂ASH₈ (stratlingite), C₄AH₁₃ and C₃ASH₆ (hydrogarnet) (Murat, 1983; Pera & Amrouz,
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1998; Wild, Khatib & Jones, 1996; Cabrera & Rojas, 2001). The primary product for calcined montmorillonite is C-S-H (Hewlett, 2003). The formation of these products, particularly the additional C-S-H gel, also helped fill up the capillary pores, contributing to a further and more important refinement of pore size. This led to a pronounced improvement in compressive strength at relatively late ages, as also shown in Figure 7.7 a), b) and c).

However, the degree of improvement in strength appeared to be highly dependent on the cement replacement level. It is known that the effect of pozzolanic reaction on strength development of concrete always becomes significant at late ages, and the 90-day compressive strengths are therefore selected for discussing that issue. In Figure 7.7 a), b) and c), it is apparent for any w/b ratio that 20 wt.% cement replacement by calcined London clay enabled the concrete to gain a compressive strength higher than either of the others (10 and 30 wt.%) on the 90-day. Should pozzolan be in abundance, pozzolanic reaction can be limited by the availability of portlandite in the system and vice versa. At 10 wt.% replacement level, pozzolanic reaction in the system appeared to be humble due to the lack of calcined London clay. In contrast, when the replacement level was 30 wt.%, there could be an excess of calcined London clay in the system, and this led to an incomplete pozzolanic reaction where portlandite was depleted with pozzolan remaining. Based on the experimental results, it is reasonable to assert that 20 wt.% was the optimum replacement level in this study.

On complete cement hydration, the formation of portlandite can vary in amount (typically 15~25 wt.\% of the reacted cement), depending on the C$_3$S and C$_2$S content (Taylor, 1997). Lothenbach & Winnefeld (2006) reported that about 0.2 g portlandite can be produced from hydrating per gram of the CEM-I they used. As the CEM-I is similar in chemical compositions to that used in this study, it is reasonable to assume that the same figure (~0.2 g portlandite per g of cement reacted) also applied in this work. Given that 1 g London clay calcined at 900 °C can consume ~0.71 g portlandite on a complete reaction, as suggested by portlandite consumption test results in Section 6.3, the ideal proportions that can ensure both a complete reaction of calcined London clay and a complete depletion of portlandite would be 78 wt.% and 22 wt.% for CEM-I and calcined London clay, respectively. This is in good agreement with the previously mentioned ‘optimum’ replacement level of 20 wt.\%.
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The comparisons between calcined London clay and other SCMs, in terms of the beneficial effect on the strength development of concretes at a w/b ratio of 0.4 and a replacement level of 20 wt.%, can be established upon Figure 7.8. The performance of calcined London clay was highly comparable to that of others at all ages. Although there may be a variation in the optimum replacement level between PFA, GGBS and silica fume, such comparisons can still provide a sense of how great the strength improvement due to the substitution by calcined London clay or other SCMs could be.
Chapter 8 CARBON SAVING ESTIMATION FOR THE USE OF CALCINED LONDON CLAY AS A SCM IN CONCRETE
8.1 Carbon saving estimation for the use of calcined London clay as a SCM in concrete

Buildings and infrastructures hold the largest share of global carbon emissions, and they have been identified with the most opportunities to reduce the emissions (Pan, 2014). It is suggested that one third of the carbon emissions around the globe can be attributed to buildings and infrastructures (Ürge–Vorsatz et al, 2007). In the UK, buildings and infrastructures are responsible for about half of the total greenhouse gas emission (BERR, 2007). The UK government has launched relevant policies with the aims of achieving ‘zero carbon’ for new homes and non-domestic new buildings from 2016 and 2019, respectively (DCLG, 2006; HM Treasury, 2008).

Buildings generate CO₂ emissions throughout their life cycles, which can typically be divided into five phases: the planning and design phase; the materials and construction process phase; the operational phase; the maintenance and renovation phase; the deconstruction and disposal phase (Ng et al, 2012). The five phases vary in the contribution to CO₂ emissions, with the operational phase being recognised as the largest, followed by the materials and construction process phase, the maintenance and renovation phase, the deconstruction and disposal phase, and the planning and design phase (Ng et al, 2012). The whole life cycle needs to be taken into account for delivering buildings towards the minimum of carbon emissions. In many developed countries, legislation has worked effectively on driving substantial reduction of CO₂ emissions from the operational phase, and subsequently, interests in the embodied carbon of construction materials have increased (Purnell, 2013). The embodied carbon of construction materials refers to the carbon emitted during the extraction and processing of raw materials as well as the transportation to construction sites (Hammond & Jones, 2008). Ng et al (2012) suggested that replacing the energy- and carbon-intensive materials with the materials requiring a significantly less amount of energy to produce can be of help in reducing the energy and carbon embodied in the buildings. Tyrer, Cheeseman & Greaves (2010) suggested that the greatest CO₂ savings can be achieved by employing SCMs to replace cement content in concrete.

The use of calcined London clay as a SCM can bring about significant savings in energy and carbon emission. This chapter is dedicated to a preliminary estimation of the amount of CO₂ that can be saved by using calcined London clay as a SCM in
The CO₂ emission associated with the production of calcined London clay is mainly derived from the combustion of fuels to support the calcining process with sufficient heat. This is not similar to the case of cement production, where the CO₂ emission can originate, primarily, from both the decomposition of calcium carbonate in raw feed and the burning of fossil fuels.

The specific heat capacity of London clay is first assumed to be identical to that of normal clays, which is 900 J/kgK (Doty & Turner, 2012). The energy required to raise one tonne of London clay to 900 °C from a drying temperature of 100 °C can be worked out as follows, where \( E \) is the energy in kWh, \( m \) is the mass of London clay in kg, \( c \) is the specific heat capacity of London clay in J/kgK, and \( \Delta T \) is the temperature change in °C.

\[
E = m \times c \times \Delta T = 1000 \times 900 \times (900 - 100) = 720 \text{ MJ} = 200 \text{ kWh}
\]

The temperature of 900 °C can be achieved by burning biomass instead of fossil fuels, and the carbon emission factor of the combustion of biomass is reportedly about 0.35 kgCO₂/kWh (Palmer et al, 2011; DECC & Defra, 2012). The amount of CO₂ emitted from the manufacture of 1 tonne of calcined London clay can, accordingly, be calculated by multiplying \( E \) with the carbon emission factor of biomass combustion, which is as follows.

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

The carbon emission of producing calcined London clay is therefore approximately 70 kgCO₂/tonne, which is about 91% less than that of cement manufacture if that is assumed to be 800 kgCO₂/tonne. Also it is comparable to 67 kgCO₂/tonne of GGBS (CSMA, 2010). A 20 wt.% replacement of Portland cement in concrete by calcined London clay would reduce the carbon emission of binders from 800 kgCO₂/tonne for 100% CEM-I to 650 kgCO₂/tonne for a blended binder. This is equivalent to an overall reduction of 18%, and a further increase to 27% can be achieved when a replacement level of 30 wt.% is adopted.

Additional energy is of course required for drying and grinding purposes, and all these have not been taken into account in this calculation.
Chapter 9 CONCLUSIONS AND FUTURE WORK
Chapter 9 Conclusions and future work

9.1 Conclusions

This research has investigated and optimized the processing required to transform excavated London clay into a SCM suitable for the use in concrete. Calcining is the key part of the processing. Excavated London clay was characterised before and after calcining at various temperatures in terms of mineralogical, structural, physical and chemical properties. The structural alteration and distortion of clay minerals due to calcining were identified. The effect of different temperatures on the pozzolanic reactivity of calcined London clay was defined, and the optimum calcining temperature determined. Concrete specimens containing London clay calcined at the optimum temperature were produced, and tested for workability and compressive strength, with results compared to concretes incorporating PFA, GGBS and silica fume. The savings in carbon emissions from using calcined London clay as a SCM in concrete have been estimated.

The key conclusions from this research are:

a) London clay is a complex mix of various clay and accompanying non-clay minerals. The clay minerals include 1:1 layer-structured kaolinite, 2:1 layer-structured illite, montmorillonite and 2:1:1 layer-structured chlorite. Goethite, pyrite, feldspar and quartz are present as non-clay minerals. The percentages of these minerals in the as-received clay were ~30.2 wt.% for kaolinite, ~11.9 wt.% for illite, ~41.3 wt.% for montmorillonite, and ~16.6 wt.% for all other phases present.

b) Calcining London clay led to oxidation, dehydration, dehydroxylation, amorphization and recrystallization, causing significant compositional and structural changes to all clay minerals and some of non-clay minerals. The degree of changes varied at different calcining temperatures.

c) The change in colour of London clay after calcining was due to oxidation of iron(II) to iron(III). XRD data confirmed that hematite was formed in calcined London clay samples.

d) Kaolinite accounted for approximately 30.2% of the as-received London clay. At 600 °C, it lost all the octahedral hydroxyl groups and became completely dehydroxylated. In addition, the tetrahedral and octahedral sheets were
puckered due to the removal of octahedral hydroxyls, leading to a collapse of 1:1 layered structure and also the transformation into metakaolin.

e) Characterization results showed that the dehydroxylation of 2:1 clay minerals (i.e. illite and montmorillonite) starts from below 600 °C and finishes at around 800 °C. Although dehydroxylation caused the octa-coordinated cations to become penta- or tetra-coordinated, the crystallinity of 2:1 clay minerals was not to be significantly affected within that temperature range. The complete distortion to the structures of illite and montmorillonite was found to take place at 900–950 °C. This indicates that dehydroxylation is not completely equivalent to amorphization in the case of 2:1 clay minerals while it is for kaolinite. The reason is possibly that 2:1 clay mineral contains considerably less octahedral hydroxyls than a 1:1 counterpart, and therefore losing those is not detrimental to the whole crystal structure.

f) The recrystallization of spinel can occur at 950 °C and above. It clearly opposed the purpose of calcining, which was to transform as much crystalline phase as possible into amorphous phase.

g) The results of pozzolanic reactivity assessment revealed that excavated London clay can be transformed into a SCM by calcining, and the optimum calcining temperature is 900 °C, followed by 850 and 950 °C. The decrease of pozzolanic reactivity at 950 °C can be attributed to the occurrence of spinel recrystallization.

h) Replacing CEM-I with up to 30 wt.% of London clay calcined at 900 °C showed no detrimental effects on workability and up to 90-day compressive strength of concrete.

i) 20 wt.% replacement appeared to be the optimum level for all the w/b ratios, with respect to compressive strength at late ages.

j) Concrete at a w/b ratio of 0.3 containing 900 °C calcined London clay gained a compressive strength higher than that of control concrete from 28 days onwards.

k) Calcined London clay was highly comparable to PFA, GGBS and silica fume as a SCM in concrete.

l) Because 900 °C is a temperature that can be readily achieved by burning low-carbon biomass rather than fossil fuels, given that calcining excavated London clay does not lead to the release of CO$_2$ from reactions, the carbon emissions
Chapter 9 Conclusions and future work

associated with the production of calcined London clay are significantly lower than those associated with Portland cement manufacture.

m) A 20–30 wt.% replacement of Portland cement by calcined London clay can produce a concrete with an 18–27 % reduction in carbon emissions.

n) This study reveals that it is technically feasible to develop London clay into a SCM suitable to be used in concrete.

o) Calcined clay, as a SCM used in concrete, has great potential in the future to compete with PFA, GGBS, particularly in the areas where these materials are in short supply.
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9.2 Future work

This research has investigated the compressive strength development of concretes containing calcined London clay over a curing period of 90 days. It is certainly worth monitoring how the gain of compressive strength can be furthered after a longer period of curing, such as 180 days and one year. Concrete specimens incorporating PFA, GGBS and silica fume were prepared identically at 20 wt.% CEM-I replacement level and 0.4 w/b ratio. However, in fact, the optimum substitution level varies among these SCMs, depending on their own features. For example, they are known as ~30 wt.% for PFA, up to ~50 wt.% for GGBS, and only ~10 wt.% for silica fume. Hence it would be more interesting to know whether calcined London clay still compares favourably with these SCMs when they are used to replace CEM-I at their own optimum replacement levels. Also the future work can focus on investigating the durability properties of concretes containing calcined London clay, as this can supplement workability and compressive strength to provide a more comprehensive performance analysis for calcined London clay as a SCM in concrete.

Apart from the above, the commercial viability of the use of calcined London clay as a SCM can be another critical research topic in the future work. The key in turning the idea into a real business lies in costs and profits rather than carbon emission savings. First of all, a pilot plant is needed to scale up the lab-based manufacturing process of calcined clay, involving pelletizing, drying, calcining and grinding. Adaption on the manufacturing process may be needed at a plant-scale to ensure the quality of the product is consistent with that achieved in the lab. The next step would be to produce calcined clay in tonne quantities and trial it in significant volumes of concrete for non-critical constructions. Economic analysis of the pilot scale production decides the business future of calcined clay.

The future work can also involve investigating the technical and commercial viability of implementing the idea in other areas around the world. The key point to this issue may largely lie in whether there is readily and locally available SCMs within that certain area.
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Figure A1 The six types of gas-adsorption isotherms suggested by IUPAC (revised from ALOthman, 2012)
Appendix

**Figure A2** The four types of hysteresis patterns on the isotherms suggested by IUPAC (revised from ALOthman, 2012)

**Figure A3** The particle morphology of 600 °C calcined London clay (×1500)
Figure A4 The particle morphology of 700 °C calcined London clay (×1500)

Figure A5 The particle morphology of 800 °C calcined London clay (×1500)
Figure A6 The particle morphology of 850 °C calcined London clay (×1500)

Figure A7 The particle morphology of 950 °C calcined London clay (×1500)
Figure A8 The particle morphology of 1000 °C calcined London clay (×1500)