

INVESTIGATION OF SANDSTONE BY-PRODUCTS AS SUPPLEMENTARY CEMENTITIOUS MATERIALS AND FINE AGGREGATE

A Thesis submitted by

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Abstract

Annually, a large volume of concrete is produced for infrastructure and housing building all over the world. Fine aggregate and cement as the main components of concrete are facing the problems of resource shortage and serious environmental pollution. It is worth noting that the output and storage of supplementary cementitious materials for preparing green concrete is facing the inability to meet the demand for clinker replacement. Recycling and value-added reutilization of industrial by-products to produce building materials to alleviate resource shortages and pollution has shown feasibility and has gradually attracted more interest.

Sandstone by-products are generated during the mining process. Different from previous studies that applied sandstone by-products as coarse aggregates, this research explored the potential of using sandstone by-products to produce and expand the sources of high-quality fine aggregate (sandstone sand) and supplementary cementitious materials (sandstone clay). One tonne of sandstone clay is produced for every 4 tonnes of sandstone sand. This thesis firstly investigated the chemical composition and physical properties of sandstone sand and thereby its application in mortar was studied. Secondly, the thermal activation mechanism and pozzolanic reactivity of sandstone clay (SC) were systematically investigated. Finally, the thermal stability of activated SC blended limestone calcined clay cement was studied.

Compared with river sand, sandstone sand exhibited better particle size distribution and similar microscopic morphology. Study found that sandstone sand contained around 15.7 % fine quartz particles smaller than 150 microns, which significantly reduced the workability. Compared with the method of increasing the water to binder ratio, adding 0.2% superplasticizer was more effective in improving the workability and achieving higher compressive strength and denser pore structure. It was found that although sandstone sand showed potential alkali silica reaction (ASR) risk, the incorporation of SCMs could significantly inhibit ASR-induced expansion. Additionally, length change caused by ASR showed a good linear relationship with the mass change, which can be used as an index to evaluate the ASR properties of fine aggregate. On the other hand, sandstone clay contains around 50 wt. % kaolinite, which was the potential source of pozzolanic reactivity. FTIR and NMR results showed that the pozzolanic reactivity of the calcined clay comes not only from the kaolinite dehydroxylation process, but also from the variation of the Al and Si coordination environments resulting from the breakage of the Si-O-Al bond. Isothermal calorimetry results indicated that, compared with active silicon, the active alumina in the metakaolin played a major role in the early hydration. Finally, according to the definition of pozzolans, three methods of pozzolanic reactivity evaluation were designed to evaluate thermally activated sandstone clay with different calcination parameters.

For the application of calcined sandstone clay, the phase evolution and microstructure development of activated sandstone clay blended limestone calcined clay cement (LC^3) at moderate temperatures (100 - 400 °C) was investigated from macroscopic, mesoscopic and microscopic. Compared with PC, LC^3 exhibited superior thermal resistance. After moderate temperature treatments, PC products were more sensitive than LC^3 in terms of length change and the generation of cracks. It was found that the open porosity of both PC and LC^3 samples increased significantly after thermal treatments due to the evaporation of free and chemically bound water and the decomposition of hydration products. Research by NMR analysis found that LC^3 samples contained longer mean chain length (MCL) and lower Si/Al ratio in C-(A)-S-H gel, which was attributed to the addition of calcined clay, resulting in producing more C-(A)-S-H. Because of presence of aluminum in C-(A)-S-H gel, LC^3 possessed superior heat resistance.

Keywords: Fine aggregate, supplementary cementitious materials, kaolinitic clay, limestone calcined clay cement, thermal stability

Certification of Thesis

This Thesis is the work of (Student name) Yubin Cao except where otherwise acknowledged, with the majority of the authorship of the papers presented as a Thesis by Publication undertaken by the Student. The work is original and has not previously been submitted for any other award, except where acknowledged. Student and supervisors' signatures of endorsement are held at the University.

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Nomenclature

General Notation:

LC^3	Limestone calcined clay cement
PC	(Ordinary) Portland cement
PPC	Portland pozzolana cement
SCM	Supplementary cementitious material
ITZ	Interfacial transition zone
МК	Metakaolin
LS	Limestone
FA	Fly ash
CC	Calcium carbonate
SC	Sandstone clay
ASC	Activated sandstone clay
SS	Sandstone sand
TGA	Thermogravimetric Analysis
XRD	X-Ray Diffraction
FTIR	Fourier transform infrared spectroscopy
NMR	Nuclear Magnetic Resonance
SEM	Scanning Electron Microscopy
PSD	Particle Size Distribution
IC	Isothermal calorimetry
XRF	X-ray fluorescence spectroscopy
Abbreviations for anhydrous	s and hydrates phases
СН	Ca(OH) ₂
C-S-H	$CaO \cdot SiO_2 \cdot H_2O$
C-A-S-H	$CaO \cdot Al_2O_3 \cdot SiO_2 \cdot H_2O$
Hc	$3CaO{\cdot}Al_2O_3{\cdot}0.5Ca(OH)_2{\cdot}0.5\ CaCO_3{\cdot}11.5H_2O$
Mc	$3CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot 11H_2O$
AFm	$3CaO \cdot (Al, Fe)_2O_3 \cdot CaSO_4 \cdot nH_2O$
AFt	$3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$

CHAPTER 1. INTRODUCTION

Human activities are increasingly causing rapid global warming, primarily owing to greenhouse gas emissions from the combustion of fossil fuels. Cement manufacturing is one of the major sources of anthropogenic CO₂ emissions, accounting for around 8% of total emissions (Hasanbeigi et al., 2012). To minimize the amount of cement consumption, replacing clinker with supplementary cementitious materials is regarded as a viable strategy for reducing the carbon footprint of cement production. Blast furnace slag, fly ash, and silica fume as SCMs are widely applied in cement and exhibit excellent performance. However, the existing SCMs cannot meet the replacement required amount of 15-30 wt. % of alternative cement. With the development of new energy technology, the output of fly ash is predicted to be substantially decreased (Environment et al., 2018).

Kaolinitic clay, a kind of layered aluminosilicate material, is a promising alternative raw material for SCMs. Under proper calcination at high temperature, kaolinite $(Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O)$ undergoes dehydroxylation to produce potentially reactive metakaolin $(Al_2O_3 \cdot 2SiO_2)$. High-quality kaolinitic clay or pure kaolin are costly and generally used as the raw materials for the paper and chemical industries. Medium-quality kaolinitic clay is extracted to make ceramics, and it is also the main raw material used by the cement industry to produce cement clinker. By-product derived low-quality clay materials are produced during the extraction of higher-quality clays or during the production of other products. Considering environmental and economic advantages, low-quality kaolinitic clays exhibit great promise as SCMs. During the process of exploring the utilization of sandstone by-products to produce fine aggregate, producing four ton of sandstone sand (S-sand) will produce about one ton of sandstone clay.

Different from traditional single calcined clay replacement, the new cement system limestone calcined clay cement can achieve up to 50 % cement replacement and possess comparable compressive strength properties with reference PC. Furthermore, LC^3 products exhibit superior performance in terms of microstructure, which can refine pore structure and increase the tortuosity of the connected pores. However, some fundamental properties of LC^3 based products are still unclear. Besides, no prior research on the effects of alkaline and curing environments on the binary system of limestone-metakaolin has been reported.

Based on fully utilizing the sandstone by-products, the aim of this research is to investigate the physico-chemical properties of sandstone sand in mortar; the activation mechanism and optimal calcination parameters of sandstone clay; the thermal stability of activated clay-based LC^3 ; and the effect of alkali and curing environments on limestone-metakaolin binary system.

In Chapter 2, the application of different kinds of fine aggregates and the research status of ASR performance of fine aggregates are first briefly reviewed. Secondly, the recent progress of utilization of activated kaolinitic clay as supplementary cementitious materials is comprehensively reviewed. In this section, the sources of low-grade kaolinitic clay, thermally activated methods, the application of activated clay in different cement systems and the relevant energy saving and economic benefits are reviewed.

Chapter 3 investigates the effects of sandstone sand as fine aggregate on the performance of mortar samples. The particle size distribution, micromorphology, compositions and impurities existing in sandstone sand are essential elements which will influence the fresh and hardened properties of mortars. In addition, the effect of around 15 % fine component smaller than 150 µm existing in sandstone sand on the fresh and hardened properties is also studied. The alkali silica reaction (ASR) property of sandstone sand is investigated and compared with river sand from the actual situation and standard requirements. It firstly finds that mass change and length change caused by ASR have a good linear relationship, which can be used as a metric to help evaluate the ASR property. The effect mechanism of ASR on compressive strength is investigated to help understand the damage process of ASR.

In Chapter 4, the thermal activation and pozzolanic reactivity evaluation of sandstone clay are studied. For low-grade sandstone clay, the effects of calcination temperature and calcination time on the dehydroxylation ratio of kaolinite are investigated to find the optimal calcination parameters. Subsequently, according to the definition of pozzolans, the methods of isothermal calorimetry test, lime consumption test and strength activity index are carried out to test the pozzolanic

reactivity of activated sandstone clay with different calcination parameters. The activated sandstone clay exhibits superior physical and chemical performance in physical filling properties and pozzolanic reactivity, respectively, which shows a good contribution to the compressive strength development.

Based on the activated sandstone clay, Chapter 5 investigates the phase evolution and microstructure development of limestone calcined clay cement (LC³) after different moderate temperature treatments (100 - 400 °C). The study aims to extend application areas of the new cement system in steam collector, radioactive waste and solid-state thermal energy storage. This chapter systematically explores the thermal stability from macroscopic, mesoscopic and microscopic. For macroscopic, the tests of length and density changes, crack generation and compressive strength change are performed. For mesoscopic, water absorption test and Scanning Electron Microscope (SEM) are conducted to evaluate the effect of different thermal treatment environments on open porosity and pore connectivity. In terms of the micro level, the evaporation of free water and chemical bound water, phase evolution and the changes in Si and Al coordination environment are characterized by thermogravimetric analysis (TGA), X-ray diffraction (XRD) and ²⁷Al and ²⁹Si NMR spectral, respectively.

In Chapter 6, the key conclusions related to this thesis are summarized. Some comments are proposed regarding the application of low-grade clays to supplementary cementitious materials. Finally, some perspectives and potential research directions are presented for the application of low-grade clay and limestone calcined clay cement.

Detailed introductions on the Chapter 3, Chapter 4 and Chapter 5 are stated in the first section of each Chapter.

CHAPTER 2. CRITICAL LITERATURE REVIEW

Note: Chapter 2.2 is based on the review paper "**Recent progress of utilization of activated** *kaolinitic clay in cementitious construction materials*", by Yubin Cao, Yanru Wang, Zuhua Zhang, Yuwei Ma and Hao Wang, published in the journal of **Composites Part B:** *Engineering*, 2021.

2.1 Fine aggregate

2.1.1 State-of-the-art of fine aggregate in concrete

Sand as the fine aggregate is an essential part of concrete. The role of the fine aggregate is to fill the gaps between the coarse aggregate and provide contribution to the strength of hardened concrete (Donza et al., 2002). Sand is the second most used natural resource, with about 10 billion tonnes being used as building material every year (Guo et al., 2020). River sand, the main source of fine aggregate, is facing the issues of overexploitation and shortage (Torres et al., 2017). In recent years, there has been a "sand shortage" in the construction industry, and the mining of river sand is difficult to meet the demand of construction industry. Excessive mining of river sand will alter river and lake bed changes, as well as the flow of regular rivers, resulting in ecological harm to the region (Dash et al., 2016). Therefore, there is a pressing need to explore environmentally friendly alternative fine aggregate.

The supply pressure of quality river sand has driven the production of artificial sand but at the cost of quality. Normal artificial sand is produced by crushing rocks, such as limestone, granite and basalt, to <4.75 mm particles and those mixtures of crushed sand and river sand. The drawbacks of artificial sand include the high-water demand to clean the fines during the manufacture process and the high-water demand in concrete mixing because of the angular shape of sand. According to previous reports, the alternative fine aggregates include recycled crushed glass (Wang et al., 2020b), recycled fine aggregate (Evangelista and De Brito, 2014), recycled plastic (Almeshal et al., 2020), sea sand, artificial sand (Nanthagopalan and Santhanam, 2011) and industrial waste (Dash et al., 2016) (e.g. foundry sand, bottom ash, copper slag, granulated blast furnace slag, etc.). Although these fine aggregates have shown feasibility in some aspects, it may adversely affect the properties of concrete. Hence, finding alternative high-quality sand to extend the sources of fine aggregates is essential.

Sandstone is a type of sedimentary rock that exists widely on the earth's surface (Pettijohn et al., 2012). It is composed of quartz grains and aluminosilicate clays. Sandstone and river sand can transform into each other under the action of natural drive (Garzanti, 2019). Sandstone can be used as construction materials to build magnificent buildings, such as church, university. However, during sandstone mining, it will produce some small pieces of sandstone and sandy clay. In the previous studies, some small-sized sandstone by-product is used as coarse aggregate in concrete and exhibits good performance (Kumar et al., 2018).

Develop process of turning sandstone by-products into sand is a way of bypassing the natural process of millennia weathering and erosion required to release it. Producing sand from crushed sandstone fragments is a practical way of utilising waste sandstone to support the construction needs of industry. With the correct georgical structure, this developed process can be replicated and is a very viable alternative source of manufactured river sand. The produced sand is delivering substantial benefits being totally organic and silt/clay free. Utilizing waste sandstone produced from an existing quarry has many advantages, such as environmentally by reducing the heavy demand on alluvial sand deposits and the need for new green field sites; economically by value adding to overall quarry operational costs.

2.1.2 Alkali silica reaction

One of the major concerns in the utilisation of sand particles in mortar or concrete is alkali silica reaction (ASR), which is a chemical reaction that occurs when the alkaline component produced by cement hydration reacts with the reactive silicon component in the aggregate to form an expansive substance, thereby causing the concrete to fracture (Shi et al., 2020). Sara et al. reported that there were three primary steps of chemical reaction in the ASR process. The three main reactions are as follows. The OH^- from cement hydration reacts with the amorphous silicon dioxide to form silicic acid and alkali silicate in the first step of ASR process (R⁺ denotes the alkali metal ions). The silicic acid formed then further reacts with OH^- and metal cations to form silicates and release water. Finally, the silicate gel

products will be released from the aggregate and react with calcium ions in the solution to form water-swellable calcium silicate gel (Glasser, 1991, Ichikawa and Miura, 2007).

$$\equiv \text{Si} - 0 - \text{Si} \equiv +OH^{-} + R^{+} \rightarrow \equiv Si - O - R + H - O - Si \equiv \text{Equation } 2\text{-}1$$

$$\equiv \text{Si} - 0 - \text{H} + 0H^{-} + R^{+} \rightarrow \equiv Si - 0 - R + H_2 0$$
Equation 2-2

$$\equiv Si - 0 - R + nH_2 0 \rightarrow Si - 0^- - (H_2 0)n + R^+$$
 Equation 2-3

In addition to aggregate reactivity, the surrounding alkaline environment, the types of alkali metal cations, serving temperature and the particle size distribution, etc. also are essential factors that affect the ASR process. Nedeljković et al. (2021) indicated that the key factor impacting the dissolution of active silica is the pH level in the pore solution. For PC products, the alkaline concentration of the pore solution is dominated by the hydration of dicalcium silicate and tricalcium silicate in the clinker. In this case, using supplementary cementitious materials (SCMs) to replace cement is considered as an effective strategy to reduce ASR (Saha et al., 2018). The reason is mainly due to the follows.

- The substitution of SCMs reduces the amount of cement needed, thereby lowering the alkali content from cement hydration.
- The addition of SCMs can react with OH⁻ generated by cement hydration to form C-(A)-S-H, which further reduces the alkali concentration of the pore solution.
- The reduction of calcium ions in solution due to SCMs consumption alters the ASR gel, thereby reducing water uptake and swelling properties of ASR products.

Multon et al. (2010) investigated the ASR expansion properties of fine aggregates with different particle sizes and found that ASR expansion decreased with the increase of the proportion of small particles. Hence, prior to application, it is critical to investigate the ASR properties of fine aggregates.

2.2 State of the art: Calcined kaolinitic clay

2.2.1 Introduction

Portland cement (PC) as the basic ingredient in mortar and concrete, has been used as the main construction material since 1824 (Liu et al., 2012, Shoubi et al., 2013). Approximately, 1.6 billion tonnes of PC and 12 billion tonnes of concrete are produced annually (Rashad, 2013a). However, the production of PC is one of the largest source of greenhouse gas (e.g. CO₂) emissions in the world, around 0.83 kg of CO₂ being generated from 1kg clinker production, accounting for around 5% of the overall CO₂ emissions (Mohammed, 2017, Mikulčić et al., 2013, Teklay et al., 2015). To reduce the CO₂ footprint, it is important to find a new potential pozzolanic material to partially or completely replace PC. A series of supplementary cementitious materials (SCMs) have been widely used, including industrial byproducts, e.g. fly ash, slag, silica fume (Wee, 2013, Suresh and Nagaraju, 2015, Khan and Siddique, 2011, Wang et al., 2020a) and natural pozzolans, e.g. natural clays and clay waste (Nehdi, 2014).

Clays refer to a series of phyllosilicates or sheet silicate minerals, such as kaolinite, smectite, illite, and montmorillonite (Brigatti et al., 2013). Among the different types, kaolinitic clay is one of the most used pozzolanic material worldwide, owing to its higher pozzolanic reactivity (Tironi et al., 2013). The key constituent in kaolinite is hydrous aluminium silicate, also denoted as Al₂O₃·2SiO₂·2H₂O. When it is subjected to proper thermal treatment, kaolinite loses its crystallinity and generates pozzolanic reactivity. It is reported that calcined kaolinitic clay possesses the highest pozzolanic reactivity compared with other calcined clays. However, the pozzolanic reactivity depends on a number of factors, e.g., calcination temperature, heating time, dehydroxylation rate, impurity ions and calcination method (Mohammed, 2017, Ferreiro et al., 2019, Kenne Diffo et al., 2015, Ghorbel and Samet, 2013, Teklay et al., 2015).

Compared with fly ash and slag, which are the current dominant SCMs used in blended Portland cement, calcined clay is regarded as the most promising pozzolanic materials in the future (Rashad, 2013b, Scrivener et al., 2018b, Zhang et al., 2016). This is related to two reasons. From one aspect, the limited supply of fly ash and slag in many regions or countries, especially in developing countries, is a barrier for the widespread utilization of these two materials (Scrivener, 2014). Whereas kaolinitic clays have abundant resources worldwide (as shown in Figure 2-1), exhibiting tremendous potential when utilized as SCM. From the other aspect, compared to fly ash and slag, the chemical composition of calcined clay is less variable. Thus, the properties of products blended with calcined clay are more predictable and controllable (Zunino and Scrivener, 2020). From a longer-term perspective, the strategy of replacing PC with calcined kaolinitic clay as feedstock material to further reduce the clinker usage has become more attractive and practical (Scrivener, 2016).



Figure 2-1. Availability of common supplementary cementitious materials (Scrivener et al., 2018b).

The application of calcined clay has been investigated in traditional PC system, as well as in novel cementitious system, e.g., limestone calcined clay cement (LC^3) and calcined clay based geopolymer system (Tuyan et al., 2018, Longhi et al., 2020, Panda et al., 2020). Figure 2-2 presents the general substitution of calcined clay in different cementitious systems. In calcined clay blended cement, the maximum replacement rate of calcined clay is around 30% without affecting performance (Paiva et al., 2012, Schulze and Rickert, 2019). LC^3 system allows a much higher level of substitution rate of clinker, which could reach 50% substitution or more, and is regarded more environmental friendly and cost competitive (Scrivener et al., 2018b, Scrivener et al., 2018a). Although calcined clay-based geopolymer can completely substitute clinker and presents a series of superiorities in mechanical properties (e.g. compressive strength) and durability (e.g. acid resistance), the higher price of activator and potential efflorescence issue limit its practical application (Zhang et al., 2016). Hence, this part will not be discussed in this thesis.



Figure 2-2. Applications of treated clay in different systems: (a) calcined clay blended cement in PC concrete; (b) limestone calcined clay cement (LC^3) in PC concrete; (c) calcined clay-based geopolymer (CCG) concrete.

As the SCM in blended cement, calcined clay not only influences the fresh state properties (e.g. workability, setting time), mechanical properties, but also improves the durability (e.g. sulfate resistance, chloride penetration and carbonation resistance, etc.) of blended cement (Rong et al., 2018). The effect of calcined clay on cement products mainly depends on a number of factors, including the chemical and mineralogical composition of the additive, amorphous phase content, the degree of dehydroxylation, specific surface area, and content of calcium hydroxide (CH) in the cement paste, the admixture content and water to binder ratio in the material (Mohammed, 2017).

Although considerable investigations have been conducted, and corresponding standards and specifications of application have been published in many countries, e.g., China (CN103459347A), Europe (NF P18-513) and America (ASTM C618-05), scientific summaries regarding the advances of kaolinitic clay-related application technique in cementitious system during the last decade are limited. This Chapter firstly review the studies conducted on the raw materials, activation process, and the pozzolanic reactivity assessment methods of calcined kaolinitic clay. Furthermore, the application of calcined kaolinitic clay in different cementitious systems is summarized with aspect to the reaction mechanism, workability, mechanical properties, and long-term durability, e.g., chloride penetration, sulfate resistance and carbonation resistance. The reaction mechanisms of each component (e.g., clinker, calcined clay, limestone) in different systems are also discussed in detail. Finally, the environmental and economic benefits of the application of calcined clay in different cementitious systems are explored.

2.2.2 Raw clay and activation processes

2.2.2.1 Sources of kaolinitic clay

Kaolinitic clay based pozzolans are available from a variety of sources, either natural minerals or industrial by-products (secondary clays). In terms of the industrial byproducts, they can be further subdivided into two categories (as shown in Figure 2-3), i) waste clays (WCs), which require activation treatment before application, e.g. the by-products from quarry manufacture, sludge from paper industries and dam sediments (Ahmad et al., 2013, Schankoski et al., 2017, Belas et al., 2014), ii) clay wastes (CWs), including broken tile, brick fragments, or ceramic wastes, etc., which have already suffered different levels of thermal treatment and possessed a certain degree of pozzolanic reactivity (Gagarin et al., 2017, Pereira-de-Oliveira et al., 2012). By reviewing previous literatures (Aglietti et al., 1986, Singh et al., 2017, Horpibulsuk et al., 2012), this kaolinitic clay could be used as SCMs in blended cement. Nevertheless, in terms of CWs, despite they possess a certain degree of pozzolanic reactivity, the properties are hard to control and have greater inconsistency, owing to the difference in thermal treatment parameters. When CWs are utilized as SCMs, they need further mechanical and thermal treatments (Awoyera et al., 2017, Prahara, 2014, Toker Derdiyok and Ergin, 2015).



Figure 2-3. Classification of kaolinitic clays.

2.2.2.2 Compositions and essential properties of clay and calcined products

It is well known that clay mineral is a mixture of kaolinite (phyllosilicate) and other passive phase crystals such as quartz, carbonates and metal oxides (e.g., iron oxide). Structurally, kaolinite is composed of one tetrahedral layer of $(Si_2O_5)^{2-}$ and one

octahedral layer of $(Al_2(OH)_4)^{2+}$, and each layer constituting the faces of the sheet (Ghorbel and Samet, 2013, Zhou and Keeling, 2013). Kaolinite is extremely stable at ambient environment (Souri et al., 2015). When it is subjected to proper thermal treatment, the mineral loses its crystallinity owing to the process of dehydroxylation and the release of active silica and alumina (Tironi et al., 2012a). The product, metakaolin (MK), is a kind of transition phase, which reserves the lamellar structure of kaolinite, while the sheet and tubular dimensions are reduced (Fitos et al., 2015). Avet and Scrivener investigated the characteristics of seven kaolinitic clays from different regions and countries, and concluded the properties varied significantly (Avet and Scrivener, 2018b). They found that the particle size distribution (D_V, ₅₀) of different clays was between 4.0-25 µm and specific surface was between 10-45 m²/g, as shown in Table 2-1. The content of kaolinite in clays from different countries or regions varies significantly from 17% to 95%.

In order to ensure the quality of clay as SCM, some important parameters must be controlled. According to ASTM C-618 (ASTM, 2003), calcined clays for class N have to fulfil both the chemical and physical requirements as shown in Table 2-2. Chemically, the content of silicon dioxide (SiO₂), aluminium oxide (Al₂O₃) and iron oxide (Fe₂O₃) should exceed 70% of the total components to ensure sufficient active components for the pozzolanic reaction. Physically, the strength activity index of calcined clay blended cement should reach 75% of the reference sample (PC).

Calcined clay	1	2	3	4	5	6	7
Original of clay	North America	South Asia	South America	South-east Asia	North America	South America	South Asia
Calcination	Flash	Furnace	Flash	Furnace	Furnace	Furnace	Furnace
Calcined kaolinite content (%)	95.0	79.4	66.2	50.3	38.9	35.0	17.0
Dv,50(µm)	5.1	5.3	4.0	10.9	8.5	23.5	5.9
BET Specific surface (m^2/g)	9.6	15.3	12.9	45.7	23.1	18.5	18.7
	XRF main comp	ositions (%)					
SiO ₂	52.0	51.8	50.3	44.9	54.7	67.6	58.4
Al ₂ O ₃	43.8	42.4	42.7	32.3	26.8	22.6	17.5
Fe ₂ O ₃	0.3	1.9	0.6	15.4	13.6	6.1	8.9
CaO	-	0.1	-	1.3	0.3	0.5	0.6
MgO	-	0.1	-	0.8	1.0	-	0.7
SO3	0.1	-	-	0.1	-	-	-
Na ₂ O	0.3	0.1	-	0.4	-	-	0.1
K ₂ O	0.1	0.1	0.1	0.2	0.4	0.3	2.3
TiO ₂	1.5	2.4	1.8	2.4	1.1	1.5	0.8
P2O5	0.2	0.1	0.1	0.4	-	-	0.1
MnO	-	-	-	0.1	-	-	0.1
Others	0.1	0.2	0.2	0.2	-	-	0.2
LOI	1.5	1.0	3.6	1.7	1.9	1.4	0.5

Table 2-1 Compositions and main characteristics of calcined clays source from worldwide (Avet and Scrivener, 2018b).

Table 2-2 Chemical and physical requirements for class N artificial pozzolanic materials.

ASTM C 618 Required content	Required indexes
Silicon dioxide (SiO ₂) plus aluminium oxide (Al ₂ O ₃) plus iron oxide (Fe ₂ O ₃),	70
min, %	70
Sulfur trioxide (SO ₃), max, %	4
Moisture content, max, %	3
Loss on ignition, max, %	10
Amount retained when wet-sieved on 45 µm (No. 325) sieve, max, %	34
Strength activity index: with PC, at 7 days, min (percent of control)	75^{*}
Strength activity index: with PC, at 28 days, min (percent of control)	75^{*}

* Meeting the 7-days or 28-days strength activity index will indicate specification compliance.

2.2.2.3 Recent progress and understanding of artificial clay pozzolans

Thermal activation

The terminology of "potential reactivity" of calcined clay refers to two aspects, i) pozzolanic reactivity (chemically reactive ability): the ability to react with a range of alkalis such as CH, in the presence of water (Hollanders et al., 2016); ii) the ability of improving microporous structure of matrix (physical improvement ability) (Walker and Pavía, 2011), especially for clays containing a number of superfinequartz. Calcination is able to convert the crystalline kaolinite to amorphous phase MK, thereby increasing the chemical reactivity of waste clay (Almenares et al., 2017, Ilić et al., 2010).

By thermally treated kaolinite in the range of 500-900 °C, the obtained MK is a metastable clay, possessing high reactivity, which is substantially an anhydrous aluminosilicate. Three types of calcination methods are used for clay calcination, i.e. rotary kilns, fluidised bed process and flash calcination. In general, a chains section is normally applied that can dry and shred the original clayey material in advance, thus avoiding the use of extra pre-processing facilities (Scrivener et al., 2018b). In rotary kilns method, the material has a residence time of around 1-2 hours in the firing chamber to ensure a good reactivity of MK (Almenares et al., 2017). The application of fluidised bed process reduces the calcination time from hours to minutes (Hanpongpun, 2019). Flash calcination takes place in special flash calciner consisting of rapid heating, calcining, and cooling processes, which is able to reduce the calcining time to seconds (0.5-12 s). In this method, the original clayey material should be dried and ground to powder in advance, and then fed to a stream of hot gas at temperatures of between 800-1000 °C (San Nicolas et al., 2013, Snellings et al., 2017). The flash calcination method enables implementation of several heat recovery

cycles, hence it has relatively high energy utilization efficiency. The authors also showed that compared with other calcination methods, MK with higher pozzolanic reactivity can be obtained by this method.

The kaolinitic clay after thermal treatment, emerged different degrees of structural collapse: the Si-O network remains essentially intact, while the Al-O network structure is reorganized due to dehydroxylation (Rashad, 2013b), which can be verified by the XRD test, FTIR test, or NMR technique, etc. (Garg and Skibsted, 2016, Fabbri et al., 2013, Uchima et al., 2015). The dehydroxylation rate (from kaolinite to metakaolin) is a major factor affecting the chemical pozzolanic reactivity of clays, as shown in Figure 2-4. The reported optimum calcination temperature for the kaolin to be converted to MK varies in different studies. The reason may partially be due to the different mineral structure of kaolin. The kaolinitic clay mineral is weathering product of feldspars. Due to the different geographical conditions and weathering conditions, the weathered products possess different crystallinity, presenting various mineral structures (Al-Ani and Sarapää, 2008). The difference in crystallinity of kaolin is mainly reflected in its hydroxyl group, which affects the optimum dehydroxylation temperature (Fitos et al., 2015). In addition, the calcination temperature, calcination duration, heating rate, calcination method and cooling method also play an important role (Zhang et al., 2009, Vizcayno et al., 2010, Mohammed, 2017). Table 2-3 summarizes some important parameters related to the clay calcination. As it can be seen that researchers reported different results on the optimum calcination temperature and heating time for clay activation.



Figure 2-4. Diagrammatic sketching model of molecular structure and dehydroxylation process of kaolinite updated from Sperinck et al. (Sperinck et al., 2011).

Generally, the clay undergoes the following processes during the calcination, as show in Figure 2-5, and the corresponding phase transition reactions are also presented below:

I. Dehydration process: the mass change from ambient temperature to 200°C is the loss of evaporative free water and organics combustion.

$$H_2 O(L) \xrightarrow{\sim 200^{\circ} C} H_2 O(g)$$
 Equation 2-4

II. Decomposition process: the gibbsite decomposition contributes to the mass loss from 200 to around 400 $^{\circ}$ C.

$$2Al(0H)_3 \xrightarrow{200 \sim 400^{\circ} \text{C}} Al_2 O_3(s) + 3H_2 O(g)$$
 Equation 2-5

III. Dehydroxylation process: from 500°C to 900°C, and the mass change is the loss of dehydroxylation of kaolinite.

$$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O \xrightarrow{500^\circ C \sim 900^\circ C} Al_2O_3 \cdot 2SiO_2(S) + 2H_2O(g)$$
 Equation 2-6

IV. Recrystallization process: it is an exothermic transition with no mass loss. The reorganization of the molecular structure of the material may occur from the

amorphous phase (MK) to the crystalline phase mullite $(3Al_2O_3 \cdot 2SiO_2)$ or spinel $(Al_2O_3 \cdot MgO)$ (Brindley and Nakahira, 1958, Alujas et al., 2015). When the calcination temperature exceeds 900 °C, the phase transition process may lead to a drop in the pozzolanic reactivity of calcined clay.

Silicon-spinel:
$$2[Al_2O_3 \cdot 2SiO_2](S) \xrightarrow{\sim 925^{\circ}C} 2Al_2O_3 \cdot 3SiO_2(S)$$
 Equation 2-7
+ $SiO_2(S)$

1:1mullite-type
$$2Al_2O_3 \cdot 3SiO_2(S) \xrightarrow{\sim 1100^{\circ}C} 2[Al_2O_3 \cdot SiO_2](S)$$
 Equation 2-8
phase: $+SiO_2(S)$

Figure 2-5 shows the different stages in the calcination process of kaolinitic clay. The best calcination temperature range for kaolinitic clay is stage V, from around 750 to 900 °C, which can lead to a high reactivity. This calcination temperature range can ensure that the kaolinite is completely dehydroxylated and the reactive component does not recrystallize. Considering the activation rate and energy consumption, calcination temperature of around 700-850 °C is normally applied (Rashad, 2013c).



Figure 2-5. Typical TGA-DTG curves of a kaolinitic clay from sandstone manufacturing.

Mechanical activation

In addition to thermal activation, mechanical ball milling is another activation method for kaolinitic clay. Ball milling can achieve partial dehydroxylation and activation of kaolin. Simultaneously, it can also achieve the granularity refinement of impurities (such as quartz) in clay to improve the physical filling ability of impurities (Vizcayno et al., 2010, Aglietti et al., 1986). Souri et al. (Souri et al., 2015) studied the differences in physico-chemical properties and chemical reactivity of kaolin obtained by mechanical activation and thermal activation. The study found that the material obtained by ball milling exhibited a certain pozzolanic reactivity. However, compared with the material obtained by thermal activation, it has a large difference in particle morphology and specific surface area. They also pointed out that thermal activation caused the coordination of Al to shift from VI to V and IV, while mechanical activation had very limited effect on Al transformation.

Sources of clays	Calcination method	Calcination temperature	Calcination duration	Heating rate	Cooling condition	Dehydroxylation rate (%)	Ref.	
Kaolin clay	Laboratory furnace	650 °C	1.5 h	-	AC ^b	97	(Ilić et al., 2010)	
Dam sludge	Furnace	600, 700, 800 °C	5 h	10 °C/min	-	-	(Chikouche et al., 2016)	
Kaolin sands	Electric muffle furnace	650 °C	1 h	-	FC ^a	-	(Janotka et al., 2010)	
Ground kaolinite	Electric furnace	500, 550, 600, 650 °C	1 h	25 °C/min	FC ^a	11, 76, 88, 91	(Taylor-Lange et al., 2012)	
Greek kaolin	Laboratory furnace	650 °C	3 h	10 °C/min	-	-	(Fitos et al., 2015)	
Paper sludge	Electrical laboratory furnace	700 °C	2 h	20 °C/min	AC^{b}	100	(Giménez et al., 2009)	
De-inking sludge	Electrical fixed-	700 750 °C	2 h	- 250 °C/h	FC ^a	100	(Pera and Amrouz,	
Water-treatment sludge	bed furnace	700, 750°C	>5 h			100	1998)	
Natural clay mineral	Gas suspension calciner	700 - 1000 °C	1.5 s	-	AC ^b	-	(Ferreiro et al., 2019)	
	Flash calciner		1.2 s	-			2017)	

Table 2-3 Comparation of the calcination parameters of different clays reported in the literature.

^a Where, FC is furnace condition, which means the calcined material is cooled in the furnace slowly until the furnace temperature reached ambient temperature; ^b AC is ambient condition, which means the calcined material is quenched to cool down rapidly to room temperature.

2.2.2.4 *Methods for assessing pozzolanic reactivity of activated clay*

The pozzolans is defined in ASTM C125-15b as: a siliceous or alumino-siliceous material which, by itself, possesses little or no cementitious value, but in finely divided form and in the presence of water, will chemically react with calcium hydroxide (CH) at ambient temperatures to generate compounds possessing cementitious properties (ASTM). According to definition, the pozzolanic reactivity assessment methods are mainly divided into two categories, namely, direct and indirect methods. The direct method is to evaluate the consumption of calcium hydroxide by pozzolanic material. The indirect method is to evaluate the materials containing pozzolanic material.

Indirect methods

Indirect methods, also known as mechanical methods, evaluate the pozzolanic reactivity of SCMs by measuring the mechanical performance. The commonly utilized method is strength activity index (SAI) by blending the pozzolans to substitute 20% - 30% of Portland cement (as shown in Equation 2-9). In the formulation of the mixture, the binder to sand ratio (b/s) and water to binder ratio (w/b) are 1:3 and 1:2, respectively (Mohammed, 2017). The strength activity index is then calculated using the equation below:

$$SAI_{(d)} = (ST_{(d)}/SC_{(d)}) * 100\%$$
 Equation 2-9

where, $SAI_{(d)}$ is the compressive strength activity index (%) at 7, 28 days; $ST_{(d)}$ is the compressive strength (MPa) of the test sample at the same curing days; $SC_{(d)}$ is the compressive strength (MPa) of the control sample at the same curing days.

The materials will be identified as pozzolanic materials with the strength activity index reached 75% (ASTM, 2003). It should be noted that the contribution to the compressive strength is the result of the coupling effect of chemically reactive ability (CRA) and physical improvement ability (PIA), which is somewhat different from only considering the pozzolanic reactivity of the material with calcium hydroxide. Aliabdo et al. (Aliabdo et al., 2014) found that clay brick powder also possessed

acceptable pozzolanic reactivity, which was proved by the strength activity index of 76.5% and 81.8%, at the age of 7 days and 28 days, respectively.

What should be noted is that the SAI results are also affected by the w/c ratio; the increase of water demand for pozzolans inevitably leads to an excess of water, which may lead to an increase in the porosity of the cement matrix and a decrease in strength.

Avet et al. (Avet et al., 2016) introduced a novel rapid, relevant and reliable (R^3) method to assess the pozzolanic reactivity of thermally treated kaolinitic clay, by testing the heat release and bound water content of the simulated system (activated clay, CaCO₃, limestone, gypsum and alkali) of LC^3 -50. The PPC30 system (30%) calcined clay and 5% gypsum of clinker) was also studied as the control system. They found a good correlation between the compressive strength and R^3 results (as shown in Figure 2-6). An improved correlation coefficient was found in both calcined clay blended systems at later curing age. The pozzolanic reactivity of calcined clay in blended cement can also be measured by the electrical conductivity test (Tironi et al., 2013) and heat evolution by using conduction calorimetry (Marchetti et al., 2018, Frankeová and Slížková, 2016).



(Normalized per gram of solid)


Figure 2-6. Correlation between relative compressive strength (20 °C) and cumulative heat released at 1 day of hydration for isothermal calorimetry run at 40 °C for systems without (top) and with limestone (bottom) (Avet et al., 2016).

Direct methods

Direct methods are based on the chemical reactivity by assessing the content of reactive components or the calcium hydroxide consumption-ability in activated clay. The amount of calcium hydroxide (CH) can be easily determined according to EN 196-2 standard. The most employed methods are Frattini test (ASTM, 2013), Chapelle test (Ferraz, 2015, Asbridge et al., 1994, Quarcioni et al., 2015) and Saturated lime (SL) test (Donatello et al., 2010), as summarized in Table 2-4. The source of calcium hydroxide in Frattini test comes from cement hydration, which is different from Chapelle test and Saturated lime test, in which calcium hydroxide is added directly. The experimental temperature in these three methods is different. Saturated lime test and Frattini test are conducted at 40°C, while Chapelle test is conducted in the boiled water. Some researchers also use TGA-DTG to determine the remaining amount of calcium hydroxide in calcium hydroxide mixed calcined clay system to evaluate the pozzolanic reactivity (Suraneni and Weiss, 2017, Hollanders et al., 2016).

Studies have shown that there is a superior correlation between the tests of Frattini and SAI (Donatello et al., 2010). Since Portland cement produces calcium hydroxide at around one-fourth of its initial weight when it is fully hydrated, the authors

attributed the correlation of the test results to the mass ratio of calcium hydroxide and pozzolanic material of 1:1. However, there is no good correlation between these tests and the SL test results. The authors pointed out that this is mainly due to the different proportions of calcium hydroxide and pozzolan (0.15:1) in the experiment, as shown in Table 2-4.

	SL Test	Chapelle test	Frattini Test	SAI test
Curing time	Not specified	16 h	8, 28 and 90 d	7 and 28d
Test temperature	40 °C	100 °C	40 °C	20 ± 2 °C
Source of CH	Saturated lime solution	Calcium hydroxide	Cement hydration	Cement hydration
CH: Pozzolan	0.15:1	1:1	1:1	1:1
Involved activity	CA	CA	CA	C-PA

Table 2-4 Comparison between tests of: Frattini, SL and SAI (Donatello et al., 2010).

CA: chemical activity; C-PA: chemical and physical activity.

Other technologies

From recent studies (Danner et al., 2018, Abo-El-Enein et al., 2019, Garg and Skibsted, 2016, Elimbi et al., 2011, Hollanders et al., 2016), a range of technical instruments are also applied to evaluate the pozzolanic reactivity of calcined clay such as thermogravimetry analysis-differential thermal analysis (TGA-DTA), X-ray diffraction (XRD), Fourier transformed infrared (FTIR) spectroscopy, Atomic absorption spectroscopy (AAS) and Nuclear Magnetic Resonance (NMR) spectroscopy. These advanced technics can help to determine the phases, molecular bonds and coordination changes in materials. Figure 2-7 presents the results tested by NMR. As the calcination temperature increases, the Al signal changes from the dominant 6-coordinated to the dominant 4-coordinated, which further increases the pozzolanic reactivity of the calcined clay by adding chemical binding sites (Alujas et al., 2015).



Figure 2-7. ²⁷Al MAS NMR spectra of uncalcined clay and calcination products (Alujas et al., 2015).

2.2.3 The application of calcined clay in blended cement system

The application of calcined clay as an additive in Portland cement has received considerable interest. The utilization of waste clay is able to minimize the consumption of PC, and thereby reduces the CO₂ emission of cement industry. In addition, the pore structure, long-term strength development and especially durability are significantly improved with the incorporation of calcined clay in PC (Mardani-Aghabaglou et al., 2014b, Tironi et al., 2012b, Mardani-Aghabaglou et al., 2014a). As such, calcined clay can be used to prolong the service life of concrete structure.

2.2.3.1 Reaction mechanism of calcined clay in blended cement system

It is well known that the major chemical reactions in calcined clay blended cement system are the hydration of C_3S and C_2S to generate CSH gel and calcium hydroxide (CH), as shown by Equation 2-10 and Equation 2-11. The hydration product of CSH gel, accounting for 2/3 of all the hydration products, is the main strength provider of the cement matrix (Foley et al., 2012). When the OPC paste reacts and hydrates thoroughly, the amount of CH makes up over 20 wt.% (Zeng et al., 2012). The presence of CH effectively improves the resistance of carbonization and acid corrosion of cement products by maintaining a high alkalinity in the cementitious system. However, the abundant CH would react with reactive components e.g.

reactive silica, silicate and carbonate from fine or coarse aggregates, and cause Alkali Silica Reaction (ASR) or Alkali Carbonate Reaction (ACR), leading to cracking and degradation (Shi and Lothenbach, 2019).

$$3CaO \cdot SiO_2 + nH_2O \rightarrow xCaO \cdot SiO_2 \cdot (n - 3 + x)H_2O + (3 - x)Ca(OH)_2$$
Equation
2CaO \cdot SiO_2 + nH_2O \rightarrow xCaO \cdot SiO_2 \cdot (n - 2 + x)H_2O + (2 - x)Ca(OH)_2Equation
2CaO \cdot SiO_2 + nH_2O \rightarrow xCaO \cdot SiO_2 \cdot (n - 2 + x)H_2O + (2 - x)Ca(OH)_2Equation

Equation
$$2-11$$

$$\begin{array}{l} Al_2O_3 \cdot SiO_2(calcined \ clay) + Ca(OH)_2(OPC \ hydration) + H_2O \\ \rightarrow CSH + CASH \end{array}$$
 Equation 2-12

When calcined clay is utilized as a partial substitute of clinker, the pozzolanic components of siliceous and aluminous can react with CH to mitigate the expansive effect of ASR and ACR. In addition, the reaction produces additional secondary cementitious compounds (SCCs), such as CSH, CAH and CASH, as shown in Equation 2-12. Previous studies demonstrated that the SCCs possess cognate properties similar to the products generated from the hydration of PC. The properties of SCCs depend basically on the MK/CH ratio (Mohammed, 2017, Murat, 1983, Bredy et al., 1988). Externally, curing temperature will also affect the rate and type of SCCs (Rojas and de Rojas, 2003). The SCCs is able to refine the microstructure of concrete, particularly in the pores and ITZ where CH are enriched. The refinement of pores and densification of ITZ can further enhance the mechanical strength and durability of concretes, and reduce capillary water absorption as well (Lagier and Kurtis, 2007).

2.2.3.2 Workability of calcined clay blended cement system

Chemically, the use of metakaolin to replace OPC will significantly reduce workability and prolong the setting time due to the high-water absorption of metakaolin. Physically, different from silica fume and fly ash, which have smooth spherical particle surfaces, the irregular particle shape of MK results in no microsphere effect. The increase of friction between the cementitious materials will exacerbate the decrease of fluidity and thixotropy (Cassagnabere et al., 2013). Therefore, additional water or high quality water reducer is needed to achieve a comparable working performance as OPC (Zhou et al., 2017).



Figure 2-8. Effect of MK content on fluidity of mortar (Jiang et al., 2015).

It can be seen from Figure 2-8 that, with same W/C ratio, the fluidity of the fresh mortar decreased with the increase of MK content (Jiang et al., 2015). This may be due to the high specific surface area and irregular micro morphology. It is reported that when the curing age was 28 days, the pozzolanic reactivity was fully stimulated; and the compressive strength was higher than that of the control group OPC. Kawashima et al. suggested that the use of nano-clay (up to 1.5% by mass of cement) accelerated the stiffening of fresh cement paste (Kawashima et al., 2012). The stiffening caused by the loss of free water is attributed to flocculation, not the adsorption of nano-clay. Paiva et al. (Paiva et al., 2012) found that rheological properties (e.g. viscosity-h and yield stress-g) of MK blended cement were sensitive with slump. As the material turned into more rigidity and less fluidity, the increase in viscosity-h or yield stress-g is reflected in the decrease in slump, exhibiting the opposite performance (in Figure 2-9). The use of high amount of superplasticizer can help to improve the workability of calcined clay blended cement-based concrete by increasing the deflocculation of MK particles, and the same suggestion also reported in (Pierkes et al., 2018, Huenger et al., 2019).



Figure 2-9. Relationship between rheological parameters and slump of pastes with various MK contents. Water content was used to keep the workability around 9 ± 1 cm slump (Paiva et al., 2012).

2.2.3.3 Mechanical properties of calcined clay blended cement

The reaction products produced by the pozzolanic reaction of calcined clay could obviously refine the microstructure of the calcined clay blended cement matrix, which in turn improve the mechanical properties (e.g., strength and modulus). For calcined clay, the percentage of metakaolin content is the dominant factor affecting the mechanical properties (Jin and Li, 2003).

Li et al. (Li et al., 2019) reported that utilizing up to 20% by volume of ceramic polishing waste as SCM to replace 33% PC in mortar, the compressive strength of 7d and 28d showed significant improvement, both of which can be increased by more than 85%. At the same time, as w/c ratios varied from 0.4 to 0.55, the workability of calcined clay blended cement is controllable and targetable, with its flowability in

the range of 226 mm to 288mm. Aliabdo et al. (Aliabdo et al., 2014) found that when the clay brick powder substitution rates increased from 5% to 25% by weight, the compressive strength reduced by 8.3% to 25.2% at the age of 28 days. However, due to the formation of secondary hydration products, the microstructure of calcined clay blended cement has been noticeably improved by reducing the pore volumes.

Microhardness testing technology provides a feasible method to quantitatively characterize the microstructure gradient of the ITZ of calcined clay blended cement paste. Duan et al. (Duan et al., 2013) applied microhardness to study the effect of SCMs (with 10 wt.% replacement ratio) on the ITZ of blended cement concrete. The study found that with the extension of the curing age, the addition of SCMs compacted the ITZ and refined the pore structure, especially for MK blended cement (in Figure 2-10). In addition, it was also found that the compressive strength of blended cement concrete had a good correlation with the average value of microhardness.



Figure 2-10. Effect of SCMs on microhardness of ITZs in blended cement concretes (Duan et al., 2013).

2.2.3.4 Durability and long-term performance

The calcined clay blended cement is proved to have a high resistance to alkali-silicon reactions, sulfate attack, chloride diffusion, and greater resistance to harmful environmental attacks (Hossain et al., 2016). Since the calcined clays could improve the pore structure and ITZ of cement matrix, the water permeability is reduced. As

water is the main medium for ion transport under the driving force of capillary water absorption and dry-wet cycles, cement with low water permeability means enhanced corrosion resistance and frost damage resistance (Wang et al., 2019b, Bao et al., 2020). The following sections discuss several durability-related issues of calcined clay blended cement mortar/concrete in detail.

Sulfate Resistance

Sulfate attack involves a series of complex physical and chemical effects. Owing to the formation of ettringite and gypsum, concrete exposed to sulfate attack is prone to cracking, expansion and exfoliation, which eventually lead to the reduction of compressive strength (Mindess et al., 2003, Güneyisi et al., 2010).

Literatures reported that the use of calcined clay as SCMs can remarkably improve the sulfate resistance of concretes (Aiswarya et al., 2013, Kirsanova and Kramar, 2015, Zhang et al., 2013). One reason is that the substitution of PC by MK reduces the quantity of tricalcium aluminate hydrates (C_3A). Another reason is attributed to the pozzolanic reaction of MK, which generate additional gel phases, filling the pores and cracks of the cement matrix, which effectively prevents the sulfate attack. In addition, the removal of calcium hydroxide generated from cement hydration lowers the quantity of ettringite formed, and effectively minimize the damage caused by sulfate attack.



Figure 2-11. Filling of pores by ettringite in samples of (a) OPC and (b) C&DWC (de Lucas et al., 2016).

Lucas et al. (de Lucas et al., 2016) studied the effect of clay-based construction and demolition waste (C&DW) as SCM on the sulfate resistance of blended cement. Study found that ettringite presented mainly in pores of cement matrix (in Figure 2-11 (a)). With 30 wt. % of activated clay replacement, the pore structure of specimens was effectively refined, and the sulfate resistance was significantly improved, as shown in Figure 2-11 (b). Güneyisi et al. (Güneyisi et al., 2010) pointed out that concrete with 20% MK can improve the compressive strength after suffering high-concentration of sulfate solution for 365 days. In addition, the investigation showed that w/c ratio played a significant impact on the sulfate resistance. Differently, Kavitha et al. (Kavitha et al., 2016) presented that the optimal incorporation ratio of

MK was 10 wt.% with respect to the sulfate resistance. Compared to PC control specimens, the weight loss of specimens blended with MK after immersing in magnesium sulphate solution was significantly reduced, as shown in Figure 2-12.



Figure 2-12. Weight loss of the OPC specimens containing 0-15% MK in a 5% magnesium sulfate solution (Kavitha et al., 2016).

Chloride ions penetration

When chloride ions intrude into the interior of cement products, it will cause pitting corrosion of the steel as long as it reached a critical concentration. Further, the expansion and rupture caused by steel corrosion lead to premature deterioration of the concrete, thereby reducing the service life of concrete structure (Zhang et al., 2017). The incorporation of calcined clay is able to improve the chloride ion diffusion resistance of concretes both from the chemical and physical aspects.

From the chemical aspect, the chemical binding effect of hydration products on chloride ions is improved by the formation of more Friedel's salt. Guo et al. (Guo et al., 2019) reported that the use of 16% MK and silica fume (SF) as SCMs, the chemical binding capacity of chloride ion of MK-blended cement paste was 6 times compared to that of SF-blended cement paste and 2 times compared to that of PC paste. This is because in MK-blended cement, the increased content of Al³⁺ from MK contributed to the formation of mono-carboaluminate. Further, the increased amount of mono-carboaluminate promoted the chemical binding of chloride ions to form more Friedel's salt by ion-exchange. As one can see from the XRD results as shown

in Figure 2-13, the mono-carboaluminate can completely convert into Friedel's salt after soaking in NaCl solution. On the contrary, Gbozee et al. (Gbozee et al., 2018) found that, considering the exposure conditions, the mono-carboaluminate did not contribute much to the chemical bonding compared to the mono-sulfoaluminate. When MK-blended cement exposed to NaCl solution at room temperature, the mono-sulfoaluminate will be completely converted to Friedel's salt and played a governing role in chemical binding of chloride ions. However, ettringite was not involved in the chemical bonding of chlorides. Marangu et al. (Marangu et al., 2018) studied the chloride ingress in a 35 % calcined clay blended Portland cement with and without the use of 0.5 M Na₂SO₄ solution replacing water. Study found that the chloride ion concentration decreased sharply in the depth of 10-20 mm, which may be due to the physical or chemical binding of cement matrix, slowing down the chloride ions penetration rate (Dousti et al., 2017). Compared to the control PC sample, PPC35 (35% calcined clay replacement) presented relatively lower chloride penetration, due to the increased amount of CSH and CAH gels generated from pozzolanic reaction (Arya et al., 1990).





Figure 2-13. (a) XRD patterns of MK or SF blended Portland cement pastes; (b) XRD patterns of cement pastes after equilibrium binding in 3 mol/L NaCl solution (Guo et al., 2019).

Calcined clay can also react with other minerals to improve the resistance of concrete to chloride penetration. Recently, Machner et al. (Machner et al., 2018b) found that the use of dolomite and MK to replace part of PC resulted in the formation of chloride-containing hydrotalcites when exposed to 2 mol/L NaCl solution. When samples were immersed in CaCl₂ solution, compared with NaCl solution, significantly more chlorides were bound in the hydrotalcite. In addition, when samples were immersed in CaCl₂ solution, the amount of chloride bound in per mole of hydrotalcite was similar to that of Friedel's salt (Machner et al., 2018a). In slag blended cementitious system, hydrotalcite was predicted to bind more chloride than Friedel's salt (Ye et al., 2016). Besides the chemical binding of chloride ions, the incorporation of MK also can decrease the chloride ingress by refining the pore structure of cement matrix (Fan et al., 2014, Ramezanianpour and Jovein, 2012).

2.2.4 The application of calcined clay in LC³

Limestone Calcined Clay Cement, also known as (LC^3) , is a novel ternary blended cement system, with limestone and calcined clay as the main constituents to replace clinker (Scrivener, 2014). One representative mixture is LC^3 -50, which consists of 50% ground clinker, 30% calcined clay (with a typical kaolinite content of 50-60%), 15% limestone powder and 5% gypsum (Scrivener et al., 2018b).

2.2.4.1 Reaction mechanism of LC^3

The hydration of clinker is still the dominant chemical reaction in LC^3 . The reactive component in calcined clay (e.g., MK) will react with portlandite to generate aluminate hydrates and gels of CSH and CA(S)H, as mentioned in section 3.1. Besides the above reaction, there are also some synergetic reactions among clinker, calcined clay, limestone and gypsum.

After calcination, the potential amorphous products of MK $(Al_2O_3 \cdot 2SiO_2)$ is generated as reactivity source of pozzolanic material, which will react with portlandite generated by the hydration of Portland cement, and produce aluminate hydrates and gels of CSH and CA(S)H, as mentioned in section 3.1. Besides the above reaction, there is also some synergetic reactions among clinker, calcined clay, limestone powder and gypsum. Different from calcined clay blended cement system, the role of limestone powder in LC³ system is essential, which will be discussed below.

Limestone powder, a by-product from the limestone quarry, has been widely applied in cement as additive and main functions are inert filler, dilution, nucleation and reactive chemical reaction (Wang et al., 2018b). In terms of the filler effect of limestone powder, it mainly depends on the particle size distribution. The finer particles can fill pores and cracks to increase the density of the cement matrix (Bederina et al., 2011, Zhang and Li, 2011). For the dilution effect, it is mainly attributed to the incorporation percentage in the cement matrix (Aqel and Panesar, 2016). Since Soroka and Stern (Soroka and Stern, 1976) first proposed the concept of nucleation of limestone, numerous literatures (Craeye et al., 2010, Tironi et al., 2017, Tennis et al., 2011) have reported that fine limestone accelerated the hydration reaction of MK and clinker (especially the C₃S) at early stage, by providing nucleation sites for the precipitation of hydration products (Wang et al., 2018b).

The presence of limestone powder ($C\overline{C}$) is conducive to the generation of hemicarboaluminate ($C_4A\overline{C}_{0.5}H_{12}$, Hc) and mono-carboaluminate ($C_4A\overline{C}H_{11}$, Mc) and the stabilization of ettringite (De Weerdt et al., 2011, Bizzozero and Scrivener, 2015). In the ternary system of LC³, limestone powder could react with the aluminate phases (from clinker or calcined clay) and CH to generate hemi- and monocarboaluminate (as shown in Equation 2-13), so as to improve the physical and chemical properties of LC^3 products (Wang et al., 2018a, Wang et al., 2018b). The addition of limestone powder also minimizes the transformation of ettringite ($C_6A\overline{S}_3H_{32}$) to monosulfoaluminate ($C_4A\overline{S}H_{12}$) phase (Equation 2-14). This is because calcium mono-carboaluminate phase and ettringite are more stable than calcium carbonate and monosulfoaluminate (Krishnan and Bishnoi, 2018). Figure 2-14 shows the different hydration products of LC^3 system at 1 day, 28 days and 90 days (Avet and Scrivener, 2018b). As one can see from the XRD results, similar amount of ettringite was observed for the reference PC and the LC^3 -50 system, after 1 day, 28 days and 90 days of hydration. Compared with 1 day of hydration, Hc and Mc products appeared in the LC^3 -50 system of 28 days and 90 days of hydration. However, in the reference PC samples, no Hc and Mc products were found.



Figure 2-14. XRD patterns of hydration for control OPC and LC³ samples at 1, 28 and 90 days (Avet and Scrivener, 2018b).

The stoichiometric formation of calcium mono-carboaluminate is considered: in the presence of excess calcium ions in pore solution, one mole of metakaolin can react with one mole of CH to generate one mole calcium mono-carboaluminate. Hence, the widely accepted blending ratio of calcined clay and limestone by weight in LC^3 formula is 2: 1 (considering 50% of metakaolin in calcined clay) (Antoni, 2013).

$$\overline{A}_{(from MK \text{ or clinker})} + C\overline{C} + 3CH \rightarrow C_3\overline{A}C\overline{C}H_{11}$$
 Equation 2-13

$$3C_4A\overline{S}H_{12} + 2C\overline{C} + H_{18} \rightarrow C_6A\overline{S}_3H_{32} + 2C_4A\overline{C}H_{11}$$
 Equation 2-14

Cement chemistry notation, \overline{A} =aluminates, A=Al₂O₃, C=CaO, \overline{C} =CO₂, CH=Ca(OH)₂, H=H₂O, S=SiO₂, \overline{S} =SO₃.

2.2.4.2 Workability of LC^3

Limestone possesses positive effect on the flowability of LC³-based materials as it can effectively reduce the flow resistance (Vance et al., 2013a). Particle size distribution and morphology of limestone are the dominant factors influencing the workability. Figure 2-15 shows the morphology of the main components, clinker, calcined clay and limestone (Muzenda et al., 2020). It can be seen from the pictures that although limestone has a larger particle size than clinker and clay, it has a smoother micro-morphology. Vance et al. (Vance et al., 2013b) investigated the rheological properties of LC³ cement pastes. The dosages of different components, limestone (10 and 20% substitution with different particle size of 0.7, 0.3 and 15 μ m), metakaolin (5 and 10% substitution), and OPC with the water to binder ratio of 0.4 and 0.45 were compared. The studies indicated that for binary or ternary mixtures containing 15 µm coarse limestone powder, the yield stress and plastic viscosity kept unchanged or decrease as the increase of cement substitution ratio. They also pointed out that in the mixture containing MK, the yield stress decreased with the increase of limestone content, regardless of the particle size of the limestone.



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(c)

Figure 2-15. Particle Micro morphology of (a) clinker, (b) calcined clay, and (c) limestone (Muzenda et al., 2020).

Owing to the presence of metakaolin, the workability of LC^3 is reduced compared with reference PC, so it is necessary to select a suitable water reducer for LC^3 system. Zaribaf, et al. (Zaribaf et al., 2015) explored the compatibility of different superplasticizers (polymelamine sulfonate, polycarboxylate ether, naphthalene formaldehyde condensate and sodium lignosulfonate) with LC^3 system. They found that polycarboxylate ether and polymelamine sulfonate superplasticizers exhibited better compatibility with LC^3 system. Similarly, Santos et al. (Santos et al., 2017) found that polycarboxylate ether superplasticizer can effectively improve the workability of LC^3 system. Nair et al. (Nair et al., 2020) studied the relationship between the superplasticizer in the paste and the amount required to achieve the target slump of the concrete mixture. As one can be seen from Figure 2-16, it was found that for LC^3 based paste and concrete, when the w/b ratio decreased below 0.40, the demand for superplasticizer suddenly increased.



Figure 2-16. Correlation between saturation dosage of polycarboxylate ether superplasticizer from paste with the finalized optimum dosages required of polycarboxylate ether from concrete (Nair et al., 2020).

2.2.4.3 Mechanical properties of LC^3

The compressive strength and shear strength of LC^3 -based, mortar and concrete were widely investigated. A range of basic experimental studies on the mechanical properties of LC^3 mortar and concrete were carried out. Compared with the conventional blended cements, LC^3 has a better mechanical performance than most binary blended cement (Cancio Díaz et al., 2017). The use of limestone and calcined clay can supply extra calcium carbonate and alumina to cement, which not only accelerate the cement hydration, but also produce more hydration products such as CSH gel, CASH compounds and carbo-aluminate hydrates (Antoni et al., 2012).

Maraghechi et al. (Maraghechi et al., 2018) found that the kaolinite content in raw clay is the dominant factor governing the compressive strength of LC^3 -based mortar or concrete. As shown in Figure 2-17 (a), the compressive strength of LC^3 in the first day was significantly lower than that of PC. With the increase of the curing age, the compressive strength of LC^3 (with kaolin content of around 40-50 % in the clay) at 7 days was comparable to that of PC. In addition, the PPC-30 (30% cement replaced by the same clay) mortar showed comparable compressive strength with LC^3 -50 at 7 days, and somewhat higher strengths at 28 and 90 days. Avet et al. investigated the

influence of various types of clays on the compressive strength of LC^3 -50 system (Avet et al., 2016). It was reported that the compressive strength was largely dependent on the kaolin content in the raw clay. As shown in Figure 2-18, clay with higher content of kaolin exhibited higher compressive strength at all ages. Similar results was also pointed out by Scrivener in (Scrivener, 2014).



Figure 2-17. (a) Compressive strength of LC^3 -50 mortars as a function of clay grade and age; (b) Comparison of PPC-30 vs LC^3 -50 mortars prepared using the same clay (Maraghechi et al., 2018).



Figure 2-18. Correlation between kaolin content in the raw clay and compressive strength (Avet et al., 2016).

Dhandapani and Santhanam (2017) compared the compressive strength of LC^{3} -50 with PC and PPC-FA30 (30% fly ash blended), as shown in Figure 2-19. They found that the compressive strength of LC^{3} -50 was lower than PC and PPC-FA30 at 3 days, but reached comparable strength at 7 days of curing age. However, at 28 days, the compressive strength of LC^{3} -50 mortars just accounted for around 2/3 of PC. This phenomenon may be related to the lower kaolin content in the raw materials. Dhandapani et al. (Dhandapani et al., 2018) studied the compressive strength evolution of two different strengths (e.g. 30 and 50 MPa) of LC^{3} -based concrete. The results showed that after 7 days moist curing, the compressive strength evolution of the two designed concretes compared with PC tended to consistency. Besides, from 90 days to 356 days, the compressive strength increased notably and was higher than that of referenced PC concrete.



Figure 2-19. Compressive strength of PC, FA30 and LC³ mortars (Dhandapani and Santhanam, 2017). 2.2.4.4 Durability and long-term performance

Chloride ions penetration

To improve the durability of mortar or concrete, it is essential to refine the micromorphology (e.g. pore radius, porosity and ITZ etc.). The refinement of pore structure particularly contributes to the formation of barrier to impede chlorides ingress, thereby protects the reinforcing steel by preventing the occurrence of chloride-induced corrosion in concrete.

It is found that the replacement of PC with limestone and calcined clay indeed could refine the pore structure of cement matrix (Avet and Scrivener, 2018b). As presented in Figure 2-20, the total porosity was notably reduced when the initial kaolinite content was higher than 38.9%. With the curing age increased from 3 days to 28 days, the pore refinement of LC^3 -50 has been further improved. The same phenomena was also reported by Avet and Scrivener (Avet and Scrivener, 2018a). Maraghechi et al. investigated the penetration depth of chloride ions in LC^3 -50 system with different kaolin content in raw clay, after soaking in 3 wt.% NaCl solution for 1 and 2 years (Maraghechi et al., 2018). They found that the erosion depth of LC^3 -50 with 50% or above kaolin content was less than 10 mm. However, the chloride erosion depth for the reference PC has already run through the mortar cube samples, as shown in the Figure 2-21. As a result of the study in (Dhandapani et al., 2018), the LC^3 system also showed similar promising resistance to chlorides.

Antoni et al. (2012) illustrated that the excellent chloride resistance of LC^3 system was related to its finer pore size distribution, while the total porosity of LC^3 was actually higher than that of PC (Antoni et al., 2012).



Figure 2-20. Refinement of pore structure of LC³-50 paste with different clay grades (figures in parentheses present initial kaolinite content of raw clay) (Avet and Scrivener, 2018b).



Figure 2-21. Chloride erosion depth of PC and LC³-50 (with different kaolinite content in raw clays) (Maraghechi et al., 2018).

The capability of chloride binding in LC^3 system is better than PC. It is widely accepted that the binding of chloride ions in cement matrix are related to the Friedel's salt or physically adsorption in the diffusion layer of CSH hydrates. In LC^3 system, the incorporation of limestone and calcined clay increases the content of calcium and aluminum and help to increase the volume of hydration products and thereby improve the binding capacity of chloride. Shi et al. (2017) indicated that the use of MK-limestone in PC increased the quantity of mono-carboaluminate during cement hydration (Shi et al., 2017). In addition, calcium was found to promote the mono-carboaluminate phases to be converted to Friedel's salt. As shown in Figure 2-22, calcium ions also help increase the chloride content in the C-S-H diffusion layer. Sui et al. (2019) found that LC^3 system possessed superiority in resistance to chloride diffusion compared with FA-limestone and slag-limestone cement systems (Sui et al., 2019). They also suggested that at least three factors (e.g. pore structure; binding capacity and pore solution) are important to the diffusion of chloride ions.



Figure 2-22. Prediction of the phase assemblages of the Portland cement (P) and MK-limestone blended cement (ML) pastes exposed to different Cl solutions (NaCl and CaCl₂). Ettr: ettringite; Mc: mono-carboaluminate; Fs: Friedel's salt; Htc: Hydrotalcite (Shi et al., 2017).

Sulfate resistance

As mentioned in section 2.2.3, the main products generated by sulfate attack in cement are ettringite and gypsum. It is well-established that by controlling the tricalcium aluminate (C_3A) content in cement, the expansion damage caused by the formation of ettringite can be significantly reduced or even avoided. In LC³ system, the combined substitution of limestone and calcined clay allows a higher replacement ratio of clinker and further reduces the C₃A content. It is also pointed out in previous study that the pore solution in LC³ system has lower pH, in which the ettringite formed is lath-like crystals and possesses less expansion. Therefore, LC³ products possess superior performance in sulfate environment.

Shi et al. (2019) studied the sulfate resistance of cement containing calcined clay and limestone immersed in 0.11 M Na₂SO₄ solution at 5 °C and 20 °C (Shi et al., 2019a). The results showed that the specimens containing calcined clay demonstrated excellent sulfate resistance (in Figure 2-23). It is believed that the pozzolanic reaction of calcined clay consumed CH, resulting in a reduction of available calcium ions to form gypsum and ettringite. Apsa and Rao (2019) investigated the sulfate resistance of LC³-based concrete immersing in 2% MgSO₄ solution for 28 days (Apsa, 2019). Study found that with the increase of calcined clay content, the sulfate resistance of LC³-based concrete was significantly improved, while the compressive strength decreased. Partial substitution of clinker by limestone and calcined clay can reduce the expansion rate and dynamic modulus loss of mortar after suffering the sulfate attack (Yu et al., 2018a). It was also pointed out that although Mc and Hc can chemically react with sulfate to generate AFt, the improvement of impermeability guaranteed the performance of sulfate resistance of LC³ products.



Figure 2-23. Visual inspection of the Specimens surface (P: Portland cement; L: limestone; ML: metakaolin and limestone; MT: calcined montmorillonite) (*Shi et al., 2019a*).

Carbonation resistance

Carbonation is another durability-related issue for reinforced concrete structure. The chemical reactions of carbonation process are demonstrated as the follows.

$$CO_2 + H_2O = H_2CO_3$$
 Equation 2-15

$$Ca(OH)_2 + H_2CO_3 = CaCO_3 + 2H_2O$$
 Equation 2-16

$$3CaO \cdot 2SiO_2 \cdot 3H_2O + 3H_2CO_3 = 3CaCO_3 + 2SiO_2 + 6H_2O$$
 Equation 2-17

Carbonation is a slow process from surface to inside, owing to the low CO_2 concentration in the atmosphere. The CH reacts with CO_2 during the carbonation process, which will lead to a reduction of pH in pore solution from 12.5-13.5 down to 8.5-9.0, and accelerate the corrosion of reinforcing steel in reinforced concrete (Marciniak et al., 2017). In LC³ system, the CH content is relatively lower buffer compared to that in Portland cement and other blended cements, hence the matrix possesses lower capability to ingress of CO_2 during carbonation. With the increase of SCMs substitution rate, the cement content decreases and the CH content also reduces. In addition, as calcined clay can react with CH to produce secondary CSH gel and crystalline phase such as C_4AH_{13} , C_3AH_6 and C_2ASH_8 , which further reduces the CH content.

Scrivener (2018) compared the carbonation resistance of different cement systems and found that the carbonation depth was LC^3 -50 >PPC-CC30 >PC after 2 years exposure, as shown in the Figure 2-24. The lighter purple of mortar matrix suggested that the CH concentration in LC^3 system was the lowest. However, other researchers reported different results. Antoni found that after 8 months of natural curing, the carbonation penetration depth was PC >LC³ >PPC-MK30 (Antoni, 2013). Similarly, Díaz et al. (2018) found that carbonation depth of LC^3 was lower than that of PCbased concrete when exposed to high and low aggressive environments (marine area and curing room) (Díaz et al., 2018). The difference in results may be due to the difference in the content of MK in the calcined clay and curing conditions.



Figure 2-24. Carbonation depths suffering 2 years of indoor and outdoor exposure for Portland cement-PC; blended cement with 30% calcined clay-PPC30; blend of 50% clinker with the same calcined clay (30%), limestone (15%) and gypsum (5%)-LC³-50 (Scrivener et al., 2018b).

Khan, Nguyen and Castel studied the carbonation of LC³-based concrete with different blends combined substitution rates (15%, 30% and 45%) and curing conditions (natural and accelerated carbonation) (Khan et al., 2018). The results showed that carbonation depth was consistently increasing with the increase of blends substitution rate. After 8 weeks of accelerated carbonation process, the carbonation depth was LC³-15 >PPC-CC30 >LC³-30 >LC³-45. What should be noticed is that the reactivity of carbonation products is higher than limestone and calcite. The carbonation products are assumed to react with excess aluminates and CH, in the presence of water, to generate Hc and Mc, and further improve the microstructure of LC³, which is worthy of further investigation.

2.2.5 Environmental and economic benefit analysis

2.2.5.1 Environmental benefit analysis

Natural resources economization

Kaolinitic clay minerals are widely distributed on the surface of the earth's crust, thus, it is one of the most abundant materials in the world (Repacholi, 2012). Further, the quality requirement of the kaolinitic clay used in cement is not as high as in other application fields (e.g. paper and cosmetics), which broadens the source of

kaolinitic clay application. Lower quality clay sources include brick wastes, paper industry sediments and miner tailings etc. In this case, the exploitation of new mine resources can be reduced. In summary, the rational and effective utilization of waste clay and tailings as SCMs not only solves the problem of waste disposal, but also minimizes the extraction of natural resources.

Energy consumption and CO2 emission

According to the review in the Sections 2.2.3 and 2.2.4, the single use of calcined clay or combined use of calcined clay and limestone can reduce the clinker usage by 30-50% while comparable properties of cementitious materials still can be achieved. The energy consumption and CO_2 emission of the three systems, namely, PC, calcined clay blended cement, and LC^3 are compared below. The following calculation is based on the formula of LC^3 -50 system. In terms of calcined clay blended cement system, 30% substitution rate is selected (Rashad, 2013c, Tironi et al., 2014, Schulze and Rickert, 2019). For PC, 90% clinker content is selected. The method used in this calculation for CO_2 emission and energy consumption is based on the Ground-to-gate system, mentioned in (Gettu et al., 2019).

Table 2-5 compares different parameters of different cement systems. It is obvious that the calcination temperature for kaolinitic clay is much lower (~800 °C) than that for clinker (1450°C), which means lower energy consumption. The advantage of calcined clay is that lower grade fuels (such as petroleum coke and even biomass) can be used to reach a relative low calcination temperature (Naqi and Jang, 2019). Compared with the production of PC, calcined clay blended cement and LC³ system save 650 and 730 MJ/tonne of fuels, respectively. Joseph et al. (Joseph et al., 2016) pointed out that the energy consumption of clay calcination was around 50% of clinker production, based on the same fuel in India. In addition, for calcined clay blended cement and LC³, CO₂ emissions is significantly reduced by 26% and 33%, respectively. According to the mineral commodity summaries (2020), the total world cement production in 2019 is around 4.1 billion tons, especially high in developing countries (e.g. China, 2.2 billion, India, 0.32 billion) (Interior and Survey, 2020). If calcined clay blended cement and LC³ systems are used instead of PC, CO₂ emissions can be reduced by 1.066 billion and 1.353 billion, respectively, each year.

For commercially calcined clay, considering the low capital investment, the existing wet clinker kiln can be retrofitted into a clay calciner. The chain section can be applied to dry and break the raw kaolinitic clay materials, therefore it could avoid the utilization for additional pre-treatment equipment (Cancio Díaz et al., 2017). Utilization of refurbished kiln to calcine clay, the energy demand is approximately 2734 MJ/tonne. Compared with the refurbished kiln calcination, the energy consumption of flash calcination is reduced by 12%, and the CO₂ emission decreases by 21%.

Category	Clinker content	Calcination temperature(°C)	CO_2 emissions, kg CO_2 eq./tonne of clay or cement	Energy demand, in MJ/tonne of clay or cement	Ref.
	-	Refurbished kiln	249	3088	(Habert et
Clay	-	Flash calciner	196	2734	al., 2010,
Clay					Habert et
					al., 2011)
LC^3	50%	~800 ^a , 1450 ^b	550	3990	(Gettu et
C^3	85%	~800 ^a , 1450 ^b	610	4070	al., 2019,
PC	90%	1450 ^b	820	4720	Cancio
					Díaz et al.,
					2017)

Table 2-5 Parameters for clay and different cements.

(a) Clay calcination temperature; (b) clinker calcination temperature; (c) C³: calcined clay blended cement.

2.2.5.2 Economic analysis

The lower temperature requirement for clay calcination, effectively saves the cost of energy consumption. In addition, the relatively low temperature required has also widened the range of fuel selections and minimized the purchase cost of fuel to a certain extent (Naqi and Jang, 2019). Relatively low kaolin quality requirements and easy availability also reduce costs from raw materials.

Table 2-6 compares the products cost and commercial price of different cements. It can be seen that LC^3 -R and LC^3 -F exhibit an obvious price advantage compared with PC and PPC. Díaz et al. (2017) and Scrivener et al. (2018) analysed the commercial feasibility of utilizing old clinker kiln to retrofit clay calciner or adopting flash calciner to burn clay. They found that both scenarios revealed better return on investment (ROI). Joseph et al. (2016) indicated that ternary LC^3 possessed comparable competitiveness with existing pozzolanic cements in India. From durability and mechanical properties, Pillai et al. (2019) evaluated the service life

and life cycle of LC^3 products compared with PC and fly ash blended PC (PC + FA) (Pillai et al., 2019). They proposed that the service life of concrete based on LC^3 system and FA blended Portland cement can be noticeably longer than that of concrete structures using only PC.

 Table 2-6 Commercial unit price and products cost. Data from: (Li et al., 2013, Cancio Díaz et al., 2017).

Materials type	Products cost (USD/t)	Price (USD/t)
LC ³ -R	61.42	108.33
LC ³ -F	56.41	108.33
PPC	66.67	108.33
PC	72.02	116.05

(a) LC³-R: clay calcination using refurbished kiln calciner; (b) LC³-F: clay calcination using flash calciner.

2.2.6 Conclusions and perspectives

2.2.6.1 Concluding remarks

The application of calcined clays as SCMs has raised remarkable interest in recent years due to its environmental and economic benefits. Calcined clay is regarded as a promising material that relieves the issue of insufficient SCMs supply. This review discussed the merits and demerits of calcined clays as SCMs in mortar and concrete. The understanding of kaolinite mineralogy, activation processes, and related chemical reaction mechanisms in different cement systems is essential to guide the application of calcined clay as SCMs in blended cement. From this review, the following conclusions can be drawn:

Through proper thermal activation from 500-900 °C, kaolin is transformed into metakaolin with high pozzolanic reactivity. According to the definition of pozzolans, pozzolanic reactivity assessment of calcined clay can be divided into two categories, direct method and indirect method. The direct method is more accurate for evaluating the pozzolanic reactivity of calcined clay. However, the indirect method can more realistically represent the role of calcined clay as SCM in blended cement.

MK reacts with CH to form SCCs which significantly alter microstructure, mechanical and durability of blended cement products. The application of calcined kaolinitic clay in blended cement can significantly improve the resistance to alkali silica reaction, chloride penetration and sulfate attack. The novel ternary system of

 LC^3 can use LC^2 up to 50% in mass. The synergistic reaction among calcined clay, limestone and clinker refines the pore structure of LC^3 , thereby enhances the mechanical strength and durability. In addition, compared with PC and calcined clay blended cement, LC^3 produces additional Hc and Mc hydration products which possess better capability to chemically bind chloride ions to generate Friedel's salt. However, the synergetic reaction also consumes a large amount of CH, which significantly reduces the pH in the pore solution and lowers the buffer effect and resistance of the LC^3 matrix to carbonation. The incorporation of normal calcined clay markedly reduces the workability of the blended cement-based mortar and concrete. This issue can be solved by the utilization of polycarboxylate water reducer. Analysis from environmental and economic aspects shows that the application of calcined clay as SCMs in cementitious construction materials also demonstrates visible benefits.

2.2.6.2 Perspectives

While there are already specifications and standards for the application of calcined clay in cement in some regions or countries, the characterization and effects of using calcined clay in cement still require more fundamental studies in the future:

- How to effectively characterize the role of calcined clay in cement products? The direct pozzolanic assessment methods focus on the ability of CH consumption. However, with the development and variation of cementitious systems (calcined clay blended cement, LC³, calcined clay based geopolymer), calcined clay not only reacts with CH in the system, but also participates in other chemical reactions with other components (e.g. limestone, sodium hydroxide, sodium silicate, etc.). Therefore, for different cementitious systems, it is necessary to find new assessment methods to evaluate the chemical reactivity of calcined clay.
- 2. For LC³, with the addition of limestone, how does phase transformation affect its performance? This is a basic question that needs to be answered qualitatively and quantitatively. It mainly involves the generation and mutual transformation of products such as AFt, AFm, Hc and Mc. Answering this question can help to understand how stable or unstable these hydration products could be, so as to optimize the mixture design and guide the development of LC³ based products with good performance or target properties.

- 3. How to define the 'right' proportion of the mixtures in LC^3 system? The weight ratio of calcined clay and limestone commonly used in LC^3 formulations is 2:1. However, the quality of clay and limestone differs greatly in different countries or regions, meaning that the reactive ingredients (kaolinite and calcium carbonate) in clay and limestone are different. Therefore, investigation on the reactive ingredients and inert impurities on the reaction process and strength development in different cementitious systems should be carried out to guide the design of LC^3 mixtures.
- 4. How to optimize the lab experiments to get results close to the practical service environment? This is not only for calcined clay but also for many studies that aim to predict long term properties. In terms of durability, most of the research are based on individual criterion (e.g. alkali silica reaction, chloride penetration, and carbonation). However, in field, cement products are usually under complex coupling environmental impacts. Therefore, more investigation on the influence of multiple coupling factors on the performance of calcined clay blended cement and LC³ is necessary in future study.

CHAPTER 3. INVESTIGATION AND DEVELOPMENT OF SANDSTONE SAND AS FINE AGGREGATE

Note: The content of Chapter 3 is based on the research paper "Recycled sand from sandstone waste: a new source of high-quality fine aggregate", by Yubin Cao, Yanru Wang, Zuhua Zhang and Hao Wang, published in the journal of Resources, Conservation and Recycling, 2022.

3.1 Introduction

Besides water, sand is the second most used natural resource on the Earth (Wesley and Puffer, 2019). Globally, 15 billion tons of sand is consumed every year, of which 10 billion tons are destined for concrete production as fine aggregate (Guo et al., 2020). The present concrete manufacturing to meet the infrastructure needs has led to unsustainable use of river sand. Of those quarried resources, such as crushed rock, sand or gravel, river sand is a rapidly diminishing resource in the world; and in fact, 'the world is in an invisible crisis of sand' (Torres et al., 2017). The construction industry world-wide is facing with a critical shortage of river sand (Wesley and Puffer, 2019, Torres et al., 2017). As a result, it is imminent to find new sources of sand to expand the sources of fine aggregates to alleviate the crisis.

In fact, there has been exploratory research on expanding the sources of fine aggregate used for building materials in the past few decades. The primary research directions are to utilize construction waste (Liu et al., 2020b, Mistri et al., 2021), glass waste (Wang et al., 2020a, Dong et al., 2021, Wei et al., 2020), industrial by-products (i.e. blast furnace slag, coal bottom ash, etc.) (Siddique, 2014, Rodriguez et al., 2009), or sea sand (Guo et al., 2020, Xiao et al., 2017). However, due to inadequate reserves, regional limits and low-quality grades, the aforementioned alternative materials are difficult to be widely used.

Another potential source of fine aggregate is manufactured sand. The supply pressure of quality river sand has driven the production of manufactured sand but at the cost of quality. Normally manufactured sand is made by crushing rocks into < 4.75 mm particles, such as limestone, granite and basalt (Bajad and Sakhare, 2018, Deshpande et al., 2012). However, manufactured sand produced by machine crushing various rocks usually leads to poor workability due to its angular and flaky

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shape (Raut and Ugale, 2016). Furthermore, when subjected to external force, the flake-shaped particles existing in concrete are prone to stress concentration, causing the concrete to crack and lowering the ultimate stress of the concrete (Zhou et al., 2020). Other drawbacks of manufactured sand include the high-water demand to clear the fines ($<150 \mu$ m) during manufacture and the high-water demand in concrete mixing because of the angular shape of sand (Nedeljković et al., 2021). Besides micro-quartz, the components smaller than 150 µm in fine aggregates containing a lot of impurities, such as clay and organic components, will influence the fresh and hardened properties of the mortar and are generally regarded as harmful components (Lanas and Alvarez-Galindo, 2003, Santos et al., 2018). So far, river sand is still the best-quality and remains as the main source of fine aggregate.

River sand is produced by the weathering and erosion of sandstone through thousands of years of natural driving forces (Garzanti, 2019). Subsequently, with the transportation of wind and rain, the liberated natural sand moves into the river and experiences the processes of scouring and sedimentation. It is then cemented together with calcium carbonate or siliceous binder under air pressure for a long period to form sandstone (Wray and Sauro, 2017). So, sandstone is actually the origin of the river sand. Sandstone, as a kind of sedimentary rock, is widely distributed on the earth's surface (Wray and Sauro, 2017). Mineral grains in sandstone are usually quartz. Sometimes the quartz content of these sands can be very high, up to 90 percent or more, which is crushed and utilised as a source of silica in glass manufacture (Bouabdallah et al., 2015). Due to their remarkable strength and durability, large blocks of sandstone are frequently utilised as building materials for the construction of historical and cultural symbolic structures, such as churches and schools (Uchida et al., 2003). Sandstone is also commonly used as concrete coarse aggregate and exhibits good performance (Kumar et al., 2017, Kumar et al., 2018). There are, however, limited studies on the performance of sandstone sand as fine aggregates. The process of turning sandstone by-products into sand is a way of bypassing the natural process of millennia weathering and erosion necessary to release it. The process to liberate natural sand particles from sandstone is crucially imminent and has demonstrated success through some pilot production plants. When sand is utilized as fine aggregate in mortar and concrete, its physical and chemical properties have a significant impact on the fresh and hardened

properties of construction products. Therefore, it is essential to conduct a comprehensive assessment of the performance of sandstone sand as fine aggregate before being widely utilised.

For the chemical property of fine aggregate, alkali silica reaction (ASR) is one of the major concerns in the application of sand particles in mortar or concrete. Shi et al. (2019) found that besides alkalis, calcium plays an important role in the ASR process, controlling the formation of ASR products. Geng et al. (2021) used in-situ 3D micro-XRD to study the micro-expansion performance of the ASR product after moisture ingress (Geng et al., 2021). The findings indicated that there was no clear swelling when relative humidity changed from 10% to 97%, which means the crystal structure change caused by humidification may not be the reason for the macroscopic concrete expansion. By studying the ASR expansion performance with fine aggregates of different particle sizes, Multon et al. (2010) found that ASR swelling decreased as the proportion of small particles increase due to the pessimum effect (Multon et al., 2010). Therefore, it is important to investigate the ASR of fine aggregates before application.

In this Chapter, the physical and chemical properties of sandstone sand were firstly characterized. The effect of sandstone sand on the workability of fresh mortar was investigated. Then the mechanical characteristics (compressive strength, flexural strength, elastic modulus) and water absorption of sandstone sand and river sand based mortars with different mix designs (sand to binder ratio, water to binder ratio and water reducer) are compared and analyzed. The effect of particles smaller than 150 μ m in sandstone sand on the performance of mortar was also studied. Finally, the evaluation of the risk of ASR and the impact of ASR on mass change and compressive strength development was investigated.

3.2 Experimental procedures

3.2.1 Materials and mixture design

The Portland cement (PC) used in this study was the Australia General Purpose Cement as classified in Australia Standard AS3972. Fly ash (FA) collected from Tarong Power station in Queensland (Australia) was used as supplementary cementitious material (SCM) in mortar mixture. Another SCM was low grade kaolinitic clay collected from Rock Trade Industry-Waterfall Quarry (Queensland, Australia). The low grade kaolinitic clay was the by-product of sandstone sand making process. The kaolinitic clay was thermally activated at temperatures of 700 and 800 °C for 1 hour to obtain activated clays (AC₇₀₀ and AC₈₀₀). The chemical compositions of materials from XRF analysis are shown in Table 3-1. FA, AC₇₀₀ and AC₈₀₀ had small (even trace) amounts of calcium content, belonging to low-calcium or calcium-free SCMs. The particle size distribution of the powder material was determined using Malvern Mastersizer 2000, and the results are shown in Figure 3-1. The main particle size distribution percentiles (D_{v50}) of PC, FA, and ACs were 20, 22, and 12 µm, respectively. Polycarboxylic superplasticizer was used as water reducer to modify the workability of the fresh mortar.



Figure 3-1. Particle size distribution of the powder materials.

There were two kinds of sand used in this research, river sand (R-sand) and sandstone sand (S-sand). The river sand was collected from Bunnings Warehouse (Australian). During the sandstone mining process, a large amount of small size sandstone rocks and sandy soil was produced. This part was collected and divided into sand and clay after being crushed and wet sieved. The sandstone sand manufacturing from sandstone was collected from Rock Trade Industry-Waterfall Quarry (Queensland, Australia) without further treatment named full component sandstone sand (FS-sand). Fine particles smaller than 150 μ m is easy to contain a significant proportion of impurities, which is generally considered hazardous (Dash et al., 2016). Hence, FS-sand was further sieved out particles smaller than 150 μ m to obtain sieved sandstone sand (SS-sand). SS-sand was further regraded according to ASTM C1260 to obtain graded sandstone sand (GS-sand) used for ASR test, as

shown in Table 3-2. The particles passing 150 μ m sieve was hereafter abbreviated as S-sand_{<150µm}. The content of silica in S-sand_{<150µm} was close to 90%, mainly in the form of nano-quartz (as shown in Table 3-1). The particle size distribution of S-sand_{<150µm} is shown in Figure 3-1.

Materials	Constituent (wt. %)										
	SiO ₂	Al_2O_3	Fe ₂ O ₃	CaO	MgO	SO_3	Na ₂ O	K ₂ O	TiO ₂	MnO	Others
PC	20.24	5.15	3.17	65.13	1.33	3.41	0.44	0.52	0.28	0.08	0.25
S- sand _{<150µm}	89.16	8.68	1.01	0.04	0.10	0.02	0.02	0.28	0.51	0.01	0.19
FA	56.86	33.95	2.88	2.71	0.66	0.14	0.42	0.76	1.91	0.06	0.25
AC ₇₀₀	66.28	29.32	2.55	0.04	0.14	0.03	0.04	0.50	0.82	0.04	0.31
AC ₈₀₀	66.09	29.31	2.65	0.04	0.15	0.02	0.04	0.53	0.83	0.04	0.32

Table 3-1 Chemical compositions of PC, fly ash and activated clay.

The first mortar mix design, shown in Figure 3-2, was utilised to compare the effects of FS-sand, SS-sand, and R-sand on workability, mechanical characteristics, and water absorption. As shown in Figure 3-2 (a), the mortars based on three sands (i.e. FS-sand, SS-sand and R-sand) were prepared with the same sand to binder ratio and water to binder ratio by mass (s/b=2.5, w/b=0.5). The impact of s/b ratios (2.5, 3.0, and 3.5) with constant w/b = 0.55 on fresh and hardened properties of FS-sand based mortars was studied, as shown in Figure 3-2 (b). Higher specific surface area of S-sand
sand
sand
sand
as shown in FS-sand might influence the fresh mortar workability. Therefore, two methods, adding additional water reducer (WR) or increase w/b ratio, were used to modify the workability of FS-sand based mortars (with constant s/b=2.5), as shown in Figure 3-2 (c-d), respectively. It should be noted that the WR was premixed in water before being added to the dry materials.




Figure 3-2. Volume proportions of representative mixes from left to right: (a) sands comparison, s/b=2.5, w/b=0.5; (b) s/b comparison, s/b=2.5, 3.0, 3.5; (c) 0.2wt. % water reducer added, s/b=2.5, w/b=0.5; (d) s/b=2.5, w/b=0.55.

Table 3-2 shows another mixture design which was based on the mortar-bar method (ASTM C1260) for the potential alkali-silica reactivity (ASR) test. According to the standard, sand used for ASR test needs to be sieved into graded sand (GS-sand), as shown in Table 3-2. The s/b and w/b ratios are 2.25 and 0.47 by mass, respectively. SCMs (i.e. FA and AC) were selected to replace 25% of PC in an attempt to adjust the potential ASR (Nguyen et al., 2020). 10% of R-sand was replaced by S-sand_{<150µm} (R₁₀-sand) to investigate the effect of fine particles on ASR. Due to the various gradations of sand, the ASR performance will differ in actual engineering applications (Du and Tan, 2014). Hence, the ASR performance of FS-sand, SS-sand, and R-sand were investigated without further gradation screening to explore ASR in practical applications.

No.	OPC	Fly ash	AM _{700°C}	$AM_{800^\circ C}$	Sand	s/b	w/b
GS-M _{OPC}	440	-	-	-	990	2.25	4.47
GS-M _{FA}	330	110	-	-	990	2.25	4.47
GS-M _{AC700}	330	-	110	-	990	2.25	4.47
GS-M _{AC800}	330	-	-	110	990	2.25	4.47
R-M _{OPC}	440	-	-	-	990	2.25	4.47
FS-M _{OPC}	440	-	-	-	990	2.25	4.47
SS-M _{OPC}	440	-	-	-	990	2.25	4.47
R ₁₀ -M _{OPC}	440				990	2.25	4.47
	GS-sand gra		_				
Sieve size (mm)	0.15-0.3	0.3-0.6	0.6-1.18	1.18-2.36	2.36-4.75	-	
Mass (g)	148.5	247.5	247.5	247.5	99.0		
Percentage (%)	15	25	25	25	10		

Table 3-2 Mixture design of mortar bars for ASR test (g).

3.2.2 Experimental procedure



The details of experimental procedure are shown in Figure 3-3.

Figure 3-3. Sample preparation procedure and experimental process.

3.2.2.1 Sand characterization

The particle size distribution and microscopic morphology of sand will affect the workability of fresh mortar and the mechanical properties of hardened mortar (Ghafor et al., 2020, Liu et al., 2020a). Therefore, the particle size distribution and microscopic morphology of the FS-sand, SS-sand, and S-sand_{<150µm} compared to R-sand were characterized before mechanical and chemical properties tests. Thermogravimetric analysis (TGA-DTG) and Fourier transform infrared spectroscopy (FTIR) tests were also carried out to identify the content of carbonate and impurities in the clay.

- The particle size distribution of the SS-sand and R-sand was determined using Malvern Mastersizer 2000.
- The apparent shape of the sand particles was observed using a Zeiss Axioplan optical microscope.
- TGA-DTG test was carried out with TA Instruments Discovery SDT 650. The temperature was increased from room temperature 23 °C up to 1000 °C at a rate of 10 °C/min in air environment.

• FTIR analysis of sand was tested using Perkin Elmer FTIR-ATR spectrometer in absorbance mode from 4000 to 400 cm⁻¹. Using absorbance values, the spectra were fitted using a baseline correction.

3.2.2.2 Sample preparation and workability test

Workability is an important property that can ensure the sand application in practice. The dry materials were weighed according to mixture design and mixed with a planetary mixer at low speed for 2 minutes. After that, water was added into the mixture and continued mixing for 3 minutes to obtain a homogeneous blend. The workability of fresh mortar was immediately tested using flow table method after mixing. To reflect the influence of sand categories and s/b ratio on the workability, multiple sets of mixes were conducted to investigate the flowability. The methods of increasing w/b ratio and adding superplasticizer were used to modify the workability.

Fresh mortar was cast in two layers into three moulds, i.e. cube $(40 \times 40 \times 40 \text{ mm})$ and cuboid moulds $(40 \times 40 \times 160 \text{ mm} \text{ and } 25 \times 25 \times 280 \text{ mm})$. Samples were demoulded after 24 h casting and immediately placed into appropriate curing conditions depending on the test. Samples for the mechanical properties and water absorption tests were cured in the controlled environmental chamber ($22 \pm 2 \text{ °C}$ and 95 % humidity) until the curing age being tested. Samples used for the accelerated expansion test were cured according to standard, and details were given in the following section 3.2.2.5 below.

3.2.2.3 Mechanical properties test

Mortars cubes $(40\times40\times40 \text{ mm})$ were used to test the compressive strength and elastic modulus by MTS universal mechanical testing machine of 100 KN at a loading rate of 1mm/min. The flexural strength was tested by three-point bending test with prism samples $(40\times40\times160 \text{ mm})$. Each value was determined by testing three specimens. The modulus of elasticity was calculated according to ASTM C469.

3.2.2.4 Water absorption test

In terms of durability, water is the main medium for the transport of corrosive substances into mortar through capillary pressure, thereby damaging the mortar structure (Cao et al., 2021a). Water absorption is regarded as a useful indicator to evaluate the microstructure and durability of mortars (Wang et al., 2019b). To better

understand the influence of sand on the pore structure and the interfacial transition zone (ITZ) between sand and cement matrix, water absorption test was conducted. To avoid pore structure damage caused by high temperature, specimens were predried at a lower temperature (60 °C) to constant weight (Zhang et al., 2017). The water absorption was evaluated by measuring the change in sample mass. The tested time intervals ranged from 0h, 0.5h, 1h, 2h, 4h, 8h, 12h, 24h, 48h, 72h, 96h, 120h, 144h, 168h and 192h. After that, the capillary water absorption (Δ W) curves can then be generated using the square root of time variation ($h^{0.5}$) (Wang et al., 2019b).

3.2.2.5 Accelerated expansion test

After demoulding, the mortar bars $(25 \times 25 \times 280 \text{ mm})$ were immersed into water heated to 80 °C for 24 hours and recorded the length as zero reading (L₀). Then the samples were transferred into 1 N NaOH solution for 28 days at 80 °C. The expansion ratio of mortar bars was accessed using the following equation:

$$\Sigma t = \frac{L_t - L_0}{L_0 - 2\Delta} \times 100\%$$
 Equation 3-1

where, Σt is the expansion ratio of mortar bar at t day(s); L_t is the length of mortar bar at t day(s); L₀ (mm) is the length of mortar bars after 24 hours water curing; and Δ (mm) is the length of expansion probe. During the expansion test, the mass of the mortar bars was measured.

3.2.2.6 Influence of ASR on compressive strength

ASR expansion could cause mortar internal damage, which further reduces the compressive strength (Gholampour et al., 2019). Hence, the effect of ASR on the compressive strength of FS-sand, SS-sand, R-sand and R₁₀-sand based mortars was investigated. The curing conditions were consistent with that of the accelerated expansion test. Cube ($40 \times 40 \times 40$ mm) specimens were cured at 80 °C water for 1 day and then transferred into 80 °C 1 N NaOH solution for 3, 7, 14 and 28 days, respectively. After curing to 3, 7, 14, and 28 days, the specimens were taken out from the alkaline solution and cooled to ambient temperature before compressive strength test. As control samples, the other two groups of samples were held at 80 °C water.

3.3 Results and discussion

3.3.1 Sand characterization

Figure 3-4 shows the particle size distribution of SS-sand and R-sand. These two sands contain no particles larger than 4.75 mm. The SS-sand is mostly distributed between 0.15 and 2.36 mm, accounting for 95.6% of the total. R-sand is mostly found in the range of 0.30 to 1.18 mm, accounting for 92.1%. SS-sand exhibits a better particle gradation than R-sand. It is worth mentioning that fine particles smaller than 150 μ m make up about 15.74% of FS-sand (as shown in Table 3-3). The particle size distribution of S-sand_{<150µm} is presented in Figure 3-1. Combined with the XRF results (as shown in Table 3-1), it can be found that the composition in S-sand_{<150µm} is mainly micro-quartz. The micro morphology of different grades of FS-sand is shown in Figure 3-5. The microscopic morphology of the S-sand is relatively round, without angular and flaky shape.



Figure 3-4. Particle size distribution characterization of two sands.



Figure 3-5. Optical microscope photos of different grades of FS-sand. Table 3-3 Gradation (mm) distribution three kinds of sand (%).

Gradation	< 0.150	0.15-0.30	0.30-0.60	0.60-1.18	1.18-2.36	2.36-4.75	>4.75
R-sand	0.19	0.55	23.97	67.42	7.61	0.26	0
SS-sand	0	26.36	30.00	21.84	17.33	4.47	0
FS-sand	15.74	22.13	25.19	18.34	14.55	3.75	0

Figure 3-6 shows the TGA-DTG results of R-sand, FS-sand and S-sand_{<150µm}. As shown in DTG curves, there are four stages of mass loss with the temperature from ambient up to 1000 °C. Stages I (< 100 °C) and II (220 - 320 °C) belong to the evaporation of free and adsorbed water, and the decomposition of gibbsite (Cao et al., 2021a). Stage III (430-750 °C) is caused by the dehydroxylation of kaolinitic clay attached on the sand surface (Fitos et al., 2015). The mass loss stage IV (500 - 750 °C) is attributed to the decomposition of carbonate phase to release carbon dioxide (Gabrovšek et al., 2006). The mass loss of R-sand and FS-sand presenting in stage III and IV are 2.2% and 1.9%, respectively. The smaller mass loss of S-sand_{<150µm} occurs at Stage III and stage IV is around 1.3%, implying that S-sand_{<150µm} containing fewer clay and carbonate components, which is consistent with the results of XRF (as shown in Table 3-1).



Figure 3-6. TGA-DTG test of R-sand, FS-sand and S-sand_{<150µm}.

To better understand the ingredients presented in the sands, FTIR analysis was performed, as shown in Figure 3-7. The hydroxyl group band at 3725-3575 cm⁻¹ belongs to characteristic peaks of inter and inner hydroxyl groups in kaolinitic clay (Cao et al., 2021a), as shown in Figure 3-7 (a). The band at 1568-1310 cm⁻¹ and 883 cm⁻¹ shows spectral interference due to the absorption of carbonate at this wavelength (Li et al., 2017). The carbonate spectrum intensity of R-sand is strong, while S-sand_{<150µm} has no clear carbonate spectrum, which is consistent with the result of TGA-DTG. The main band at 1230-893 cm⁻¹ is the typical stretching vibrations of Si-O-T band, where T = Si or Al. FS-sand, SS-sand and S-sand_{<150µm} exhibit clear Si-O-Al band at 1005, 939, 913 and 532 cm⁻¹, which is due to the presence of kaolinitic clay. There is a peak shifting (around 1020 cm⁻¹) of the main band at 1230-893 cm⁻¹ in FTIR spectrums of R-sand compared with S-sand, which is caused by higher Si/Al ratio (as shown in Figure 3-7 b) (Longhi et al., 2020). R-sand shows a broad hump with less kaolin characteristic peaks, suggesting less clay composition.

All in all, FS-sand has a good particle gradation, and contains 15.7% of S-sand_{<150µm}. The major component of S-sand_{<150µm} is quartz, with a little amount of kaolinitic clay. However, compared with FS-sand, R-sand contains more carbonate component and less kaolinitic clay.



Figure 3-7. FTIR of four different types of sand: R-sand, FS-sand, SS-sand and S-sand<150um.

3.3.2 Workability analysis

Figure 3-8 shows the photograph of the fresh mortars during flowability test and the detailed flowability results of each mortar are shown in Figure 3-9. The flowability of R-sand based mortar is approximately 205 mm. And SS-sand based mortar has a considerable fluidity with R-sand based mortar around 200 mm. At constant w/b and s/b ratios, the flowability of FS-sand based mortar is reduced by 23% compared to SS-sand based mortar, which is ascribed to the presence of S-sand_{<150µm}. The presence of S-sand_{<150µm} increases the specific surface area and tends to increase the surface water absorption at the initial stage (Liu et al., 2020b). Adding a suitable superplasticiser (0.2% of binder) or increasing the w/b ratio (0.55) can effectively improve the fluidity of FS-sand based mortar, as shown in Figure 3-9. However, it has been shown that increasing w/b ratio causes a bleeding phenomenon on the mortar surface, as shown in Figure 3-8 (e). Hence, superplasticiser is preferable for improving workability.



Figure 3-8. Flowability photograph of fresh mortars.

It is known that s/b ratio could significantly affect the workability performance of the fresh mortar. While keeping the consistent w/b ratio, the flowability of FS-sand based mortar decreases significantly with the s/b ratio increasing from 2.5 to 3.5 (as shown in Figure 3-9). As the s/b ratio increases, the percentage of cement content in the mortar decreases. It is reported that fresh cement paste wrapping on the sand surface can minimise the friction between the sands, so that the fresh mortar has a better fluidity (Zhang et al., 2018). The higher water absorption of impure clay may also be responsible for the reduction in workability. Although a higher s/b ratio has a good water retention effect and can minimise water loss, it reduces the workability and will affect the microstructure development of hardened mortar (Zhao et al., 2020).



Figure 3-9. Flowability of fresh mortars with different w/b, s/b and superplasticiser.

3.3.3 Mechanical properties

3.3.3.1 Compressive and flexural strength

The compressive strength and flexural strength of mortars after 28 days of standard curing are shown in Figure 3-10, together with the error bars. With the constant w/b and s/b ratio, SS-sand based mortar shows higher compressive strength than the mortars based on R-sand and FS-sand. FS-sand based mortar shows comparable compressive strength to R-sand based mortar even though it has a poor flowability. The sand particles cannot expand freely under the constrained pressure from surrounding cement paste and other fine particles, which contributes to strengthening the ultimate stress of transverse cracking (Safiuddin et al., 2018). This indicates that FS-sand with better particle gradation is more conducive to obtain higher strength. It could be found that the flowability of fresh mortar will affect the compressive strength development of hardened mortar.

After improving the workability, the compressive strength of FS-sand based mortar is significantly improved. According to Figure 3-10 (a), the compressive strength of FS-sand based mortar with 0.2 wt. % superplasticiser is 53 MPa, which is 51% and 23% greater than that of R-sand and SS-sand based mortars, respectively. As one can see, the utilization of superplasticiser is more conducive to the compressive strength development than increasing the w/b ratio. The compressive strength of FS-sand based mortar shows a similar decreasing trend as flowability with increasing s/b ratio.

As shown in Figure 3-10 (b), the R-sand based mortar shows the lowest flexural strength around 7.2 MPa, while the highest flexural strength of 8.9 MPa is observed in FS-sand based mortar with 0.2% superplasticiser. Compared with compressive strength, the flexural strength among different mortars has minor fluctuation.



Figure 3-10. Compressive and flexural strength of mortars with different s/b and w/b ratios at 28 days.

Figure 3-11 shows the development of compressive and flexural strength of mortars with comparable workability at 7, 14 and 28 days. The compressive strength of samples at 7 days and 14 days are approximately 75% and 92% of that at 28 days, respectively (as shown in Figure 3-11 (a)). This is consistent with previous research, which the development of compressive strength is mainly concentrated in the first14 days (Kim et al., 1998). As illustrated in Figure 3-11 (b), FS-sand and SS-sand based mortars reach similar flexural strength 9 MPa at 28 days. It is worth noting that the compressive and flexural strengths of FS-sand and SS-sand-based mortars during the entire curing period are higher than those of the control group.



Figure 3-11. Compressive and flexural strength of mortars at 7, 14 and 28 days (s/b=2.5, w/b=0.5).

3.3.3.2 Modulus of elasticity in compression

Elastic modulus is one of the important mechanical properties that determines strain and creep behaviour (Zhang and Wang, 2016). The stress-strain curve and elastic modulus of mortars are presented in Figure 3-12 (a, b). After reaching the ultimate stress, the stress drops sharply, indicating that brittle failure has occurred (Kumarappa and Peethamparan, 2020). All mortars exhibit brittle failure with little or no softening behaviour prior to complete failure, which is consistent with the previous results (Thomas and Peethamparan, 2015). This is related to the fact that mortar is a rigid material. The ultimate strain of mortars is significantly different, while the failure curve is comparable. A significant difference in the strain corresponding to the ultimate stress is observed in mortars, whereas the difference in stress and strain in the process of reaching the ultimate stress is very small. There is a compaction process before the specimen is evenly loaded, as shown in Figure 3-12 (a). Therefore, the stress and strain at the end of compaction are taken as zero reading. The secant slope at 0.4 times of ultimate stress point (0.4 (f'_c - f_{c0})) is defined as the elastic modulus of mortar (Li et al., 2018).



Figure 3-12. (a) Stress-strain curves of mortars; (b) elasticity modulus of mortars.

Figure 3-12 (b) shows the elastic modulus of mortars with different mixture design. The elastic modulus of mortars is between 11.5-14.6 GPa. The type and gradation of the aggregate will affect the modulus, because the deformation produced in the mortar is related to the elastic deformation of the aggregate (Saikia and De Brito, 2012). The elastic modulus of FS-sand based mortar is lower than SS-based and R-sand based mortars with the same s/b and w/b ratios. This may be due to the poor workability of the FS-sand based mortar under the same w/b ratio, resulting in a larger deformation caused by the porous microstructure of the hardened mortar (Arandigoyen and Alvarez, 2007). The use of a superplasticiser and a higher w/b ratio can assist in increasing the elastic modulus by densifying the microstructure. As the s/b ratio increases, the elastic modulus tends to decrease, which is consistent with the strength results.

3.3.4 Water absorption analysis

The amount of absorbed water of mortars with different mixture design is presented in Figure 3-13. The water absorption rate decreases with time, and the water absorption mainly occurs in the early stage within 7 h^{0.5}, which reaches about 86% of the total water absorption at 15 h^{0.5}. The amount of absorbed water of R-sand, SSsand and FS-sand based mortars are similar, while FS-sand based mortar shows relatively lower value. This indicates that although the presence of S-sand_{<150µm} reduces the workability of FS-sand based mortar, it can play a better filler role and densify the pore structure to promote the formation of a denser structure of hardened mortar.

Figure 3-13 (b) shows the water absorption performance of FS-sand based mortar after using superplasticiser and increasing the w/b ratio to improve workability. The mortar with 0.2% superplasticiser shows the lowest amount of water absorption. It indicates that proper improvement of the workability of fresh mortar by superplasticiser is helpful to refine the pore structure and open porosity (Ahmad et al., 2019). However, the mortar with increasing w/b ratio shows a higher water absorption and faster water absorption ratio at early stage. This is because that the additional water in mortar resulting in higher open porosity after low temperature drying (60 °C). Hence, in order to prepare mortar with good durability, the method of using water reducer is more suitable for improving the workability.



Figure 3-13. Amount of absorbed water of mortars with different mixture design.

3.3.5 Alkali silica reaction analysis

3.3.5.1 ASR of GS-sand based mortar bars

Figure 3-14 displays the cumulative change value of length and mass of GS-sand based mortar bars for 28 days. The cement hydration is substantially completed after 24 hours water curing at 80 °C. Hence, the increase in length and mass of the mortar bars is attributed to the penetration of the alkaline, the generation of ASR products and the water absorption of the ASR products. The length of GS-M_{OPC} sample shows a continual increment with curing time. The calculated expansion ratio at 14 days (i.e. Σ_{14}) of GS-M_{OPC} sample is around 0.14% (between 0.10% and 0.20%), which

means that the ASR risk is uncertain as per ASTM C1260. Furthermore, extending the curing time to 21 and 28 days, the expansion ratio increases to 0.17% and 0.25%, respectively.

However, the application of 25% of supplementary cementitious materials, such as fly ash and activated kaolinitic clay significantly reduces the expansion. After curing for 14 days, the expansion ratio of GS-M_{FA}, GS-M_{AC700} and GS-M_{AC800} samples are 0.02%, 0.02% and 0.01%, respectively. ASR starts from the dissolution of reactive silica in sands, and the alkali concentration in pore solution is a governing factor affecting the dissolution of reactive silica (Lindgård et al., 2012). In SCMs blended cement, the pozzolanic reactive components of silicate and aluminate in fly ash and calcined kaolinitic clay could react with OH⁻, and thereby mitigate the ASR effect by reducing the pH value of pore solution (Wei et al., 2019). The replacement of PC by SCMs reduces the amount of cement content, which can further reduce the amount of OH⁻ produced by cement hydration.

The pozzolanic reactivity between SCMs and portlandite can reduce the Ca^{2+} concentration and change the ASR products, effectively reducing the expansion stress of the ASR product by reducing the viscosity and yield stress of the ASR product (Saha et al., 2018). The increased reactive Al content from SCMs is also reported that can encapsulate reactive SiO₂, which hinders the dissolution of reactive fine aggregate (Shafaatian, 2012). In view of above results, it is found that although GS-sand showing potential uncertain ASR risk, using appropriate SCMs to replace cement can effectively inhibit the expansion.





Figure 3-14. The cumulative change value of (a) length and (b) mass of mortar bars derived from GSsand at OPC system and OPC-SCMs blended system during accelerated expansion test for 28 days.

Figure 3-14 (b) shows the mass change of GS-sand based mortar bars. The cumulative mass change of GS-M_{OPC} sample continually increases with the increase of curing age. However, the mass change of the mortar bars with SCMs replacement is relatively lower and mainly occurs in the first 10 days. It is noted that the mortar bar of GS-M_{FA}, GS-M_{AC700} and GS-M_{AC800} samples exhibit a relatively significant mass increment while minor length change. This might relate to the difference in ASR products and the water absorption capacity of ASR products (Shi et al., 2019b). The application of SCMs promotes the formation of C-S-H or C-(A)-S-H gel rather than silica gel during ASR process, while the former products has lower water absorption capacity (Shi et al., 2019b). The densified microstructure by the application of SCMs might be another reason, restricting the expansion stress caused by ASR products. Comparing Figure 3-14 (a) and (b), it can be concluded that although SCMs blended cement mortar undergoes ASR reaction, the ASR products in blended cement show lower expansion property.

3.3.5.2 ASR of practical sand-based mortar bars

In order to compare the resistance of S-sand and R-sand in practical applications to the ASR damage, expansion and mass change analysis on ungraded sand based mortar bars were conducted, as shown in Figure 3-15. R-M_{OPC} sample shows the highest length change, while the FS-M_{OPC} sample shows the least length change. This suggests that FS-sand based mortar bar shows the best resistance to expansion caused by ASR, while the R-sand based mortar bar shows the biggest expansion due to the ASR. This might be also due to the effect of fine particles in FS-sand, resulting in a denser structure. The expansion of R₁₀-sand based mortar bars is smaller than that of R-sand based mortar bars, which also confirms that the presence of S-sand_{<150µm} can effectively decrease expansion caused by ASR (Joo and Takahashi, 2021).

It can be found that the length change of mortar bars at the first 4 days is relatively slow, while the mass change increases fast. This may be due to the penetration of alkali solution entering the interior of the mortar in the first 4 days, which is mainly affected by the mortar microstructure. During this period, the ASR reaction is relatively slow. After 4 days, the length change increases quickly due to the ASR expansion and the mass increases slowly due to the water absorption of ASR products. After reaching 20 days, the increase in the length and mass of mortar bars gradually slow down, entering the late stage of the ASR reaction. The mass change shows the same trend as length change, as shown in Figure 3-15 (b).





Figure 3-15. The cumulative change value of (a) length and (b) mass of mortar-bars derived from FSsand, SS-sand, R-sand, and R_{10} -sand at OPC system during accelerated expansion test for 28 days.

In view of the above results, FS-sand, SS-sand, R-sand, and R₁₀-sand based mortar bars exhibit different degree of length and mass changes caused by ASR. However, the S-sands (i.e. FS-sand and SS-sand) show a better resistance to expansion caused by ASR comparing with R-sand. Comparing Figure 3-15 (a) with (b), it can be found that compared with the mass change, the difference in expansion change is more significant. This may be due to FS-M_{OPC} and SS-M_{OPC} samples possess a better microstructure.

3.3.5.3 Correlation between expansion and mass change

Figure 3-16 shows the fitting relationship between length and mass change of mortar bars. It can be found that there is a better linear relationship between the length change and mass change. Shi et al. (2020) studied the influence of alkaline environment (KOH and NaOH) and curing temperature (60 and 80 °C) on ASR, and also found a rough relationship between the length change and mass change within ten weeks curing. The data at the first 4 days has a significant influence on the correlation formula, resulting in a linear (y = a + bx) or exponential ($y = \exp (a + bx + cx^2)$) relationship. The fitting formula of each sand is shown in Figure 3-16. The length change and mass change of GS-sand based mortar bar show a significant exponential relationship with R-Square of 0.989. This indicates that there is a significant mass increase at the first 14 days, but smaller length change. FS-sand based mortar bar shows the similar exponential relationship with R-Square of 0.995.

R-sand, SS-sand and R_{10} -sand based mortar bars display a linear relationship, the coefficients of *x* are 0.142, 0.123 and 0.159, respectively. The data of FS-sand with mass change over 4 g could be fitted as a linear relationship with coefficients of 0.114. Smaller coefficient suggests smaller length increment with same mass increment. Hence, FS-sand shows the least expansion, followed by SS-sand, R-sand and R_{10} -sand. As known, ASR expansion usually starts at the interfacial transition zone (ITZ), between cement matrix and sand (Lindgård et al., 2012). When facing the expansion stress caused by the same quality ASR products, the mortar microstructure formed by FS-sand and SS-sand shows better resistance to the expansion stress.

The data points from mortar bars are summarized in Figure 3-16 (f). The distribution of points is concentrated in the area shown in the figure, with upper limitation line (y = 0.143x) and lower limitation (y = -0.646 + 0.154x). In view of above results, it could conclude that there is a better relationship between the mass change and length of mortar bars. As the measurement of mass change is simpler and more convenient than the determination of length change, the linear relationship between length and mass change can be used as a supplement index for evaluating the risk of ASR for sand. However, the influence of the particle size distribution of sand and the pore structure of mortar on the relationship between length and mass change needs to be further explored.







Figure 3-16. The fitting relationship between length and mass change of (a-e) GS-sand, R-sand, SS-sand, FS-sand and R₁₀-sand based mortar bars for 28 days accelerated expansion test, and (f) the trend-lines obtained considering all data points for all mortar bars.

3.3.5.4 Effect of ASR on compressive strength

Figure 3-17 shows the compressive strength of mortar samples under different curing environments, i.e. 1N sodium hydroxide solution at 80 °C and water curing at 80 °C. The compressive strength of control samples cured in water increases with the curing age. After water curing for 29 days, FS-sand based mortar shows the highest compressive strength, followed by SS-sand, R_{10} -sand and R-sand. This suggests that the fine particles in S-sand promote the formation of denser microstructure and higher compressive strength, which is consistent with the former results (Ahmad and Chen, 2018). The compressive strength of samples soaked in alkaline solution is lower than that of control samples and declines with the extension of curing age. This is due to the formation of cracks caused by the expansion of ASR process, which are prone to stress concentration when subjected to external pressure (Thomas, 2011). The compressive strength of mortars based on R-sand, R₁₀-sand and SS-sand reduces by 9.2, 7.8 and 7.2 MPa, respectively, after 14 days alkaline curing. It should be noted that the compressive strength first decreases and then slightly increases, but it is still lower than the control sample. Similar results were also observed in (Yazıcı, 2012). After 28 days of alkaline curing, the FS-sand based mortar still shows the highest residual compressive strength, whereas the mortar based on R-sand has the lowest. In view of above results, the SS-sand and FS-sand based mortars have a smaller decrement in compressive strength under alkaline curing, indicating that they are more resistant to ASR than R-sand.

By comparing Figure 3-10 and Figure 3-17, it is clear that the compressive strength of mortars under 80 °C water curing is relatively lower than that under standard curing. Same results are also reported in (Hu et al., 2019). A possible explanation is that the high temperature curing accelerates the cement hydration rate at earlier age and prevents the distribution of hydration products, which reduces the efficiency of filling and distribution of hydration products in pores at later ages (Aldea et al., 2000, Ba et al., 2011). In addition, the water vapor pressure generated by high temperature water curing may also result in the formation of micro-cracks between the sand and the paste matrix, which will also reduce the compressive strength (Ozawa et al., 2019, Yazıcı, 2007).



Figure 3-17. Compressive strength of mortar samples after water and 1N NaOH alkaline curing.

The effect of ASR products on the microstructure development of mortars is schematically shown in Figure 3-18. Before soaking in alkaline solution, the cement hydration in mortar is almost completed by soaking in 80 °C water. There are hydration products, i.e. calcium hydroxide (CH) and calcium (alumina) silicate hydrate (C-(A)-S-H), distributing in the ITZ zone, as shown in Figure 3-18 (a). The expansion stress generated by the hydration products (f_o) and the confinement stress generated by the cement matrix (f_{co}) reach a balance, resulting in a stable state of ITZ.

After soaking in 1N alkaline solution, external OH⁻ enters the interior of the mortar, resulting in the increase in alkali concentration in ITZ and the generation of ASR products, as shown in Figure 3-18 (b). This leads to the generation of expansion stress (f_a) caused by the water absorption of ASR products. The total internal stress (f_o+f_a) gradually increases and becomes greater than the confinement stress (i.e. f_o+f_a), causing the formation of cracks in the cement matrix and ITZ. During this period, the compressive strength of the mortar reduces as the microstructure deteriorates. As the curing age increases, the continuously generated ASR products spread to the whole ITZ space and fill the cracks, as shown in Figure 3-18 (c). Hence, the compressive strength of mortars increases slightly and presents corrugated reduction, as shown in Figure 3-18 (d). Similar phenomenon caused by sulfate attack were also reported in (Yu et al., 2018b).



Figure 3-18. Schematic diagram of the mechanism of ASR attack in mortars, (a) samples before ASR test, (b) samples exposed to ASR test for 14 days and (c) samples exposed to ASR test for 28 days, (d) schematic diagram of strength drop.

3.4 Conclusions

In this chapter, the workability, mechanical property, water absorption and ASR risk of mortars prepared with sand from different sources were investigated. It shows that the S-sand produced from sandstone by-product can be used as high-quality fine aggregate. This research highlights that the application of S-sand as fine aggregate, on the one hand, realizes the value-added reuse of waste sandstone resources, and on the other hand, it could help relieve the shortage issue of dwindling river sand and reduce the mining of river sand. Specific conclusions can be drawn as following:

1. S-sand possesses smoother microscopic morphology and better particle size gradation with around 15.7% of fine sand smaller than 150 μ m, which reduces the flowability of the fresh mortar, due to its higher water absorption. Appropriate increase of w/b ratio or application of superplasticiser can significantly improve the workability, and the latter is considered more suitable to avoid the bleeding issue.

- Compared with R-sand and FS-sand, SS-sand without the <150 µm fines shows superior performance in compressive and flexural strength at the same w/b ratio and s/b ratio. However, the mechanical properties of FS-sand mortar are greatly enhanced after improving workability by increasing w/b ratio or adding superplasticiser.
- FS-sand, SS-sand, and R-sand mortars exhibit similar water absorption properties when mixed at the same w/b and s/b ratios. The application of superplasticiser could significantly reduce the water absorption of FS-sand mortar by refining the microstructure.
- 4. Even though GS-sand shows potential ASR risk, the application of SCMs (i.e. fly ash and activated clay) could satisfyingly reduce the expansion. The expansion of FS-sand and SS-sand based mortar bars is less than that of the river sand, indicating that sandstone sand mortar having better resistance to ASR. The strong linear relationship between length change and mass change is found in this study, which could be used as an alternative evaluation index for ASR risk.

CHAPTER 4. INVESTIGATION AND DEVELOPMENT OF SANDSTONE CLAY AS SCM

Note: The content of Chapter 4 is based on the research paper "**Turning low grade kaolinitic** sandstone clay into supplementary cementitious material: Activation and pozzolanic reactivity evaluation", by Yubin Cao, Yanru Wang, Zuhua Zhang, Yuwei Ma and Hao Wang, published in the journal of **Composites Part B: Engineering**, 2021.

4.1 Introduction

Concrete is one of the most widely used material in the world. It is the far most important material for construction industry. Portland cement (PC) is the dominant cementitious material in concrete, which acts as a glue to bind coarse and fine aggregates together (Chi et al., 2019). To meet the rapid construction development, it is estimated that about 4.1 billion tonnes of PC are produced annually, especially in developing countries such as China (2.2 billion) and India (0.32 billion) (Rashad, 2013a, U.S.D.o.t., 2020). The production of large amounts of OPC is energy and emission intensive due to the high temperature calcination (1450 °C) and decarbonation of limestone (Marchon et al., 2013). The production of PC is accounting for 5-8% of man-made greenhouse gas into the atmosphere (Jang et al., 2016). In the past decades, researchers and industry attempt to reduce the environmental impact of cement production by improving the calcination efficiency of coal and exploring alternative clean fuel to lower the environmental impact of cement clinker production. However, calcination efficiency and alternative clean fuel based strategies are reaching a bottleneck of optimization (Alujas et al., 2015). Another strategy is to find supplementary cementitious materials (SCMs) to partially replace clinker. The application of SCMs has demonstrated significant potential and proved to be a promising alternative to change the existing status.

Given the continuous demand of cement in the coming decades, the source of SCMs needs to be sufficiently available. Some industrial by-products (e.g. fly ash and blast furnace slag) have been widely utilized as SCMs, but the expected annual output or existing storages of these materials cannot cater to the increasing requirement (Scrivener, 2014, Shen et al., 2020). Although some materials (e.g. volcanic ashes) possess pozzolanic property and exhibit good potential as SCMs, they are difficult to

be supplied and applied globally due to geographical constraints (Rodriguez-Camacho and Uribe-Afif, 2002).

The utilization of thermally activated kaolinitic clay as SCM is receiving increasing interest due to its sufficient reserves and wide distribution. After calcination at 600-900 °C, kaolinitic clay is thermally activated and transforms from crystalline kaolin into amorphous metakaolin (MK) through the dehydroxylation process. MK usually has high pozzolanic reactivity. During PC hydration, MK reacts with calcium hydroxide, water and/or sulfates to form C-(A)-S-H, ettringite and AFm-phase (De Silva and Glasser, 1990). Scrivener et al. (Scrivener et al., 2018b) proposed a ternary cement system (limestone calcined clay cement, LC³), replacing the clinker by limestone and calcined kaolinitic clay. The LC³ system expands the substitution ratio of clinker to 50%.

The high grade or purified kaolinitic clay is expensive and is often used in paper and chemical industry. High grade kaolinitic clay is also the raw material for the production of clinker and ceramics. Clay with kaolin content of about 40-60% is usually defined as low grade kaolinitic clay (Scrivener et al., 2018a, Avet and Scrivener, 2018b, Dixit et al., 2021, Alujas and Martirena, 2015, Alujas et al., 2015). Considering the utilization and economic benefits, low grade kaolinitic clay has great potential as SCM (Avet and Scrivener, 2018b). Previous investigations on low grade kaolinitic clays included dam silt, marine sediment, and paper industry sediments (Du and Dai Pang, 2018, Wang et al., 2013). Although studies on the activation of low grade kaolinitic clay as SCMs increase gradually, there is still no report on low grade kaolinitic clay with a wide distribution and large storage. The construction industry world-wide is facing a critical shortage of river sand (Torres et al., 2017). Due to the homology with river sand and the large storage and wide distribution, sand produced from sandstone shows great advantages as a fine aggregate. However, during the sandstone sand production process, producing one ton of sandstone sand will generate about one ton of sandstone clay. The possibility of expanding the source of SCMs is made possible by the production of a large amount of sandstone clay.

The aim of this chapter is to systematically explore the feasibility of thermal activation of waste sandstone clay from sand production into SCM. The optimal activation parameters of the clay mud were investigated. This study is mainly

divided into three parts: the first part, which is covered in this chapter, is the characterization of activated muds, followed by the pozzolanic reactivity assessment and the practical function in mortars. The dehydroxylation ratio (TGA-DTG), functional group change (FTIR), crystal phase change (XRD), and the alternation of Al and Si coordination environments (NMR). The pozzolanic reactivity of the activated mud was comparatively assessed from two aspects: isothermal calorimetry and lime consumption capacity. The actual role of activated sandstone clay in mortar was evaluated by mortar strength test. This study will provide certain guidance for the future application of low-grade kaolinitic clay as SCM for construction industry.

4.2 Experimental procedures

4.2.1 Materials

The raw material (sandstone clay, SC) used in this research was collected from Rock Trade Industry - Waterfall Quarry (Queensland, Australia), which was rich in kaolin and quartz fines. The sandstone clay was the by-product produced by sand manufacturing from sandstone. The colour of the SC appeared yellow owing to the presence of iron oxide (Hernández et al., 2020). PC was supplied by Australia cement industry. The chemical composition of the SC and PC was tested by X-ray florescence using a Bruker AXS S4 Explorer spectrophotometer operating at a power of 1 kW and equipped with an Rh X-ray source, as shown in Table 4-1. According to the component analysis, the SC meets the requirements of SiO₂ + Al₂O₃ + Fe₂O₃ > 70%, SO₃ < 4%, moisture content less than 3% and loss on ignition less than 10%, which could be classified as Class N pozzolanic material (ASTM, 2003).

4.2.2 Thermal activation

Before thermal treatment, the SC was wet sieved through 32 µm sieve. The thermal activation of SC was carried out in a laboratory furnace with heating rate of 800 °C/h. The SC was heated from the ambient temperature up to 600 °C, 700 °C, 800 °C and 900 °C, respectively. The time of residence at each designed temperature was 1, 2 and 3 h, respectively. The obtained activated sandstone clays (ASCs) were designated as ASC₆₀₀₋₁, ASC₆₀₀₋₂, ASC₆₀₀₋₃, ASC₇₀₀₋₁, ASC₇₀₀₋₂, ASC₇₀₀₋₃, ASC₈₀₀₋₁, ASC₈₀₀₋₂, ASC₈₀₀₋₃, respectively. The chemical composition of ASC₇₀₀₋₁ and ASC₈₀₀₋₁ obtained by X-ray florescence are shown in

Table 4-1. The chemical compositions of ASCs were consistent and therefore ASCs at 600 °C and 900 °C were not tested.

Oxide	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	TiO ₂	MnO	LOI.
PC	20.24	5.15	3.17	65.13	1.33	3.41	0.44	0.52	0.28	0.08	0.25
50	(2.00	24.61	2.04	0.22	0.21	0.04	0.02	0.00	0.25	0.04	7.64
SC	62.00	24.61	3.24	0.33	0.31	0.04	0.02	0.60	0.85	0.04	/.64
ASC ₇₀₀₋₁	66.28	29.32	2.55	0.04	0.14	0.03	0.04	0.50	0.82	0.04	0.24
ASC ₈₀₀₋₁	66.09	29.31	2.65	0.04	0.15	0.02	0.04	0.53	0.83	0.04	0.30
Class N		>70%				<4%					<10%

Table 4-1 XRF compositions of materials characterised by XRF, wt. %. LOI is loss on ignition at 1000 °C.

After thermal activation, the ASCs were moved outside of furnace and cooled at ambient temperature in order to prevent crystallization of amorphous components (Ilić et al., 2010, Souri et al., 2015). The particle size distributions of ASCs were measured with Microtrac S3000/S3500 laser beam granulometer, allowing measurements of particles sizes ranging from 0.024 to 2800 microns in dispersion. As shown in Figure 4-1, the particle size of samples reduces significantly after thermal activation. The median diameter (D_{50}) of SC is 51.75 µm and the ASCs are around 18.5 µm. The particle size distribution of the ASCs is consistent.



Figure 4-1. Particle size distribution characterization of the SC and ASCs.

4.2.3 Characterization techniques

Thermogravimetry (TGA-DTG) test

Powder samples were used to do thermogravimetry analyses (TGA-DTG) test to determine the initial kaolin content in the SC and the conversion ratio of kaolin to metakaolin in the ASCs (Fernandez et al., 2011). Before TGA-DTG test, the SC was pre-dried at 60 °C oven for 24 hours. TA Instruments Discovery SDT 650 was used to test the TGA-DTG data at a heating rate of 10 °C/min from ambient temperature to 1000 °C in the nitrogen condition.

Dehydroxylation ratio: During thermal activation process, the gibbsite $(Al(OH)_3)$ and kaolin $(Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O)$ are the main initial reactants in the SC. The rupture and loss of hydroxyl groups in these reactants form active aluminium oxide (Al_2O_3) and metakaolin $(Al_2O_3 \cdot 2SiO_2)$ in ASCs, as shown in Equation 4-1 and Equation 4-2. The conversion ratio of kaolin to metakaolin determines the pozzolanic reactivity of ASCs. The weight percentage of kaolin in the SC and ASCs could be calculated by Equation 4-2 and Equation 4-3 by Tangent method. The details for Tangent method could be found in (Scrivener et al., 2018c). The Tangent method could minimize the influence of impurities present as secondary phases in the raw materials on the quantification of kaolin (Avet and Scrivener, 2018b). The conversion ratio of kaolin in ASCs could be calculated according to Equation 4-4.

Gibbsite:
$$2Al(OH)_3(s) \xrightarrow{\sim 200-340 \, \circ C} Al_2O_3(s) + 3H_2O(g)$$
 Equation 4-1

Kaolin:
$$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O(s) \xrightarrow{\sim 460-720 \, \circ C} Al_2O_3 \cdot 2SiO_2(s) + 2H_2O(g)$$
 Equation 4-2

$$wt.\%_{kaolin} = \frac{Mol_{kaolin} \times wt.\%_{H2O}}{Mol_{H2O}} \times 100\%$$
 Equation 4-3

$$DH_{T, H} = (1 - \frac{Wt.\%_{kaolin in ASCs}}{Wt.\%_{kaolin in SC}}) \times 100\%$$
 Equation 4-4

where, *wt.* $\%_{kaolin}$ is the weight percentage of kaolin $(Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O)$ in the SC and ASCs; *Mol_{kaolin}* and *Mol_{H2O}* are the molecular weight of kaolin and water, respectively; *wt.* $\%_{water}$ is the weight of lost water caused by dehydroxylation of kaolin; *wt.* $\%_{kaolin in SC}$ is the weight percentage of kaolin in the SC; *DH_{T, H}* is the

conversion ratio of kaolin to metakaolin in the ASCs which after heat treatment at temperature *T* (i.e. 600, 700, 800 and 900 °C) and duration *H* (i.e. 1h, 2h and 3h).

Scanning electron microscopy (SEM)

The morphological aspect of SC and ASCs was observed by Scanning Electron Microscopy (SEM, Hitachi SU3500) on powder samples mounted on the holder and coated with gold films using a JEOL smart coater. Analyses were made at 700 and 10000 magnifications at 5-15 kV with lower accelerator energies for imaging with secondary electron returns only. Samples were pre-dried at 60 °C oven for 24 hours and gold-coated for 2 minutes before test.

Dissolution test

In order to further observe the morphology of the material, the dissolution test of the SC and ASCs was conducted by preparing suspension using deionised water (liquid to solid ratio = 5:1). According to the standard ISO 10390: 2005 (ISO, 2005), the mixtures were shaken for 5 min and allowed to stand for 3 hours to reach equilibrium. The pH value of the mixtures was also determined by a pH electronic tester (Standard, 2005).

X-ray diffraction (XRD)

XRD patterns were collected between 5 and 65° 2 θ with a step size of 0.02° 2 θ , applying Cu K α radiation of wavelength 1.54 Å, voltage 40 kV and current 40 mA. Jade 6 powder diffraction file (PDF) database was used to analyse the diffraction patterns.

Fourier transformed infrared (FTIR)

FTIR test was carried out using a PerkinElmer FTIR spectrometer in absorbance mode from 4000 to 400 cm⁻¹ to determine the characteristic bands in SC and ASCs. Before carrying out the FTIR test, SC was pre-dried at 100 ± 5 °C for 24 hours.

MAS NMR analysis

MAS NMR test was carried out to analyse the coordination bond shift of ASCs. The spectra were collected on a Bruker 300 MHz Avance III 400 WB spectrometer with

double air bearing 4 mm MAS probe. Samples were spined at 8 KHz with 1 us pulse (pi/12) and 1 s relaxation period between scans. Peak position was also verified with CPMAS spectrum. Repetition delay was 100 s, which was sufficient for complete relaxation. Up to 1000 scans were collected. Peak deconvolution was carried out with PeakFit, applying a part of SigmaPlot. The minimum number of peaks was used to enable an accurate and meaningful interpretation of the spectra and peak full width at half height was restricted to ≤ 4 ppm.

4.2.4 Mortar strength test

Mortar samples were prepared with 30% ASCs replacement of PC according (Avet et al., 2016, Alujas et al., 2015, Tironi et al., 2013, Fernandez et al., 2011). The curing method was modified. For compressive strength test, $4 \times 4 \times 4$ cm³ cubic samples were prepared with 1:3 binder to sand ratio (b/s) and 0.5 water to binder ratio (w/b). Two control groups were prepared, i.e. PC without substitution as control group I (M_{OPC}), 30% of SC substituted PC as control group II (M_{SC}). The mix design was shown in Table 4-2. The specimens were demolded after 24 hours ambient curing, and then sealed with polyethylene film and moved into curing chamber (20 ± 2 °C) until 7 and 28 days. The compressive strength test was carried out using an MTS universal mechanical testing machine with a loading speed of 1.0 mm/min. Strength activity index (SAI) was calculated according to Equation 4-5,

$SAI_{(d)} = (ST_{(d)}/SC_{(d)}) * 100\%$

Equation 4-5

where, $SAI_{(d)}$ (MPa) is the compressive strength index at 7, 28 days; $ST_{(d)}$ (MPa) is the compressive strength of ASCs blended cement based mortar at the same curing age; $SC_{(d)}$ (%) is the compressive strength of the control sample I (PC based mortar) at the same curing age.

		SAI-test	IC test	LC test	
Composition (g)	SAI-PC	SAI-SC	SAI-ASCs	IC-ASCs	LC-ASCs
PC	450	315	315	157.5	-
ASCs	-	-	135	67.5	40
Water	225	225	225	112.5	100

Table 4-2 Mixture formulation of SAI test, IC test and LC test.

SC	-	135	-	-	-
Sand	1350	1350	1350	-	-
Lime	-	-	-	-	60*

60*: measured by TGA test, the main component calcium hydroxide is 89.21 wt. %, and calcium carbonate was 5.68 wt. %.

4.2.5 Pozzolanic reactivity test methods

Isothermal Conduction Calorimetry (ICC) method

The rate of heat evolution and cumulative heat of all the mixtures were measured by an isothermal conduction calorimeter (TAM-Air-314, TA Instruments Ltd., New Castle, NE, USA). Prior to the experiment, the calorimeter was calibrated at 25 °C, and the materials (PC and ASCs) were stored at 25°C for 24 h. During isothermal calorimetry test, the amount of solid materials is fixed. In the testing procedure, raw materials (100% PC and 70% of PC + 30% ASCs) were firstly mixed with the distilled water for 1 min, and then 10 ± 0.01 g paste sample was carefully poured into a glass ampoule and transferred into the calorimeter channel. The whole procedure lasted for about 3 min. The heat flow was recorded, and the cumulative heat was calculated up to 7 days.

Lime consumption (LC) method

The lime consumption (LC) method was designed based on the reaction between ASCs and the hydration product (i.e. $Ca(OH)_2$) of PC. The reactive metakaolin in ASCs could react with calcium hydroxide, forming calcium silicate hydrate (C-S-H) and aluminium-substituted C-(A)-S-H hydrate. As known, the pH value of the saturated calcium hydroxide solution at 20 ± 2 °C is around 12.65, which is similar to the pH of the pore solution in hydrated PC (Plank and Sachsenhauser, 2009, Vollpracht et al., 2016). The initial weight percentage of calcium hydroxide in lime-ASCs mixture is around 56.05 wt. %. The calcium hydroxide in reacted lime-ASCs paste could be calculated by TGA-DTG test with Tangent method (Ilić et al., 2010). It should be noted that the calcium carbonate in lime-ASCs pastes is from lime and the carbonation of calcium hydroxide during sample preparation and solidification. In view of this, calcium carbonate formed in the sample will also be accounted into unconsumed calcium hydroxide that has not participated in the pozzolanic reaction.

Then the lime consumption amount and consumption percentage could be calculated by Equation 4-6 and Equation 4-7.

$$wt.\%_{consumption} = 56.05\% - \left(\frac{Mol_{CH} \times wt.\%_{H20}}{Mol_{H20}} + \frac{Mol_{CH} \times wt.\%_{CO2}}{Mol_{CO2}}\right) \times 100\%$$
 Equation 4-6
wt.%_{consumption}

$$P_{consumption} = \underbrace{wt. \%_{initial}}_{e} = \underbrace{\frac{56.05\%}{Mol_{H2O}} \left(\frac{Mol_{CH} \times wt. \%_{H2O}}{Mol_{H2O}} + \frac{Mol_{CH} \times wt. \%_{C2O}}{Mol_{C2O}} \right) \times 100\%}_{56.05\%}$$
Equation 4-7

Where, 56.05% is the initial weight percentage of calcium hydroxide content in lime-ASCs paste, *wt.* $\%_{consumption}$ is the weight percentage of calcium hydroxide consumed by the pozzolanic reaction; *Mol_{CH}*, *Mol_{H2O}* and *Mol_{CO2}* are the molecular weight of calcium hydroxide, water and carbon dioxide, respectively; *wt.* $\%_{H2O}$ and *wt.* $\%_{CO2}$ are the weight percentage of lost water and carbon dioxide caused by decomposition of calcium hydroxide and calcium carbonate in TGA-DTG test, respectively; *P_{consumption}* is the consumption percentage of calcium hydroxide by the pozzolan reaction.

The details of LC test are addressed below. The ratio of ASCs to lime was 2:3, while the ratio of solid to water was 1:1. The mixture formulation is shown in Table 4-2. The solid materials were first mixed for 2 minutes, and the water was added into mixture for another 4 minutes stirring. The fresh blends were cast in sealed containers for 24 hours. After being demoulded, samples were sealed and cured in the standard curing room $(20 \pm 2 \text{ °C})$ for 7 and 28 days, respectively. The cured samples were immersed in alcohol solution for 24 hours to terminate the hydration and then dried at vacuum oven at 50 °C for 6 hours before TGA-DTG test.

4.3 **Results and discussion**

4.3.1 Thermal activation analysis of SC

The mass change and derivative mass change of the SC during thermal activation process are presented in Figure 4-2. The mass loss occurred below 200 °C is mainly caused by the release of free and adsorbed water. The mass loss happened after 200 °C could be divided into two stages, i.e. stage I from 200 to 340 °C and stage II from 460 to 720 °C. The mass loss of stage I is about 1.14% which is attributed to the

transformation of gibbsite (Al(OH)₃) to reactive Al₂O₃ (Yusiharni and Gilkes, 2012). According to Equation 4-1 and Equation 4-3, there is around 3.29 wt. % of gibbsite in the SC. The mass loss of stage II from around 460 to 720 °C is around 6.14%, which is due to the dehydroxylation of kaolinite. According to Equation 4-2 and Equation 4-3, the initial kaolin content in the SC is around 44 wt. %. There is a platform ranging from 544 to 621 °C for derivative mass change, which might relate to the energy required for the dehydroxylation of the inter-hydroxyl and innerhydroxyl in kaolin (Sperinck et al., 2011). In view of the results, the calcination temperature for the SC needs to exceed 700 °C to obtain the optimal conversion rate of kaolin to metakaolin. However, when the temperature is higher than 900 °C, the amorphous metakaolin would transfer to Al₂O₃- γ and mullite, reducing the pozzolanic reactivity of ASCs (Alujas et al., 2015).



Figure 4-2. TGA-DTG test of raw sandstone clay.

4.3.2 Characterization of ASCs

4.3.2.1 Morphology analysis

Figure 4-3 shows the microscopic morphology of the SC and ASC₉₀₀₋₁. Comparing to the SC (Figure 4-3 a), the ASC₉₀₀₋₁ has a certain physical agglomeration (Figure 4-3 b). The agglomeration might be caused by the overlapping of loose metakaolin flakes. There is no agglomeration phenomenon found from the particle size distribution of the ASCs, as shown in Figure 4-1. After calcination, the particle size of ASCs becomes smaller than SC. This may be because the samples tested for
particle size distribution were carried out under water-soluble conditions. It is speculated that when the ASCs are dissolved in water, the agglomeration phenomenon of the material is alleviated. The dissolution test will be discussed later. It is observed from Figure 4-3 (c) that the kaolin in the SC is a dense layered structure before calcination. After calcination, the obtained metakaolin in the ASC₉₀₀₋₁ remains the layered structure but becomes loose, as shown in Figure 4-3 (d). This is caused by the dehydroxylation of the inter-hydroxyl and inner-hydroxyl in kaolin (Sperinck et al., 2011).



Figure 4-3. Micrographs of SC (a, c) and ASC₉₀₀₋₁ (b, d) from SEM test.



Figure 4-4. pH values of SC and ASCs. "R." is raw SC; and "D." is distilled water.

Figure 4-4 shows the pH values and dissolved state of the SC and ASCs in distilled water. The measured pH value of distilled water (i.e. D.) is 6.12, which presenting weakly acidic, while the pH value of the SC in distilled water (i.e. R.) is 6.76. SC is a neutral material and distilled water is easy to absorb CO₂ from air to form H₂CO₃ releasing H⁺. The presence of soluble salts in the SC alleviates the impact of CO₂ and increases the pH value of the solution. The pH values of ASCs in distilled water are lower than distilled water, except for the ASC₉₀₀₋₃ (i.e. 6.54). The ASC₇₀₀₋₁ displays the lowest pH value, i.e. 5.53. In general, the influence of calcination temperature and heating time on pH value is minor. Hence, after replacing OPC with a large percentage of SCM, the ASCs themselves will not have a significant impact on the alkaline environment of the blended cement system.

As shown in the visual inspection of the ASCs in distilled water (Figure 4-4 right), all solutions present a reddish brown. This might attribute to the phase change of iron oxide. Natural clay presents light yellow due to the existing of ferric oxide (Fe₂O₃·H₂O). Experiencing high temperature calcination, ferric oxide dehydrated and transformed to ferric oxide, presenting reddish brown (Ghorbel and Samet, 2013). The solutions of ASC₆₀₀₋₁, 2, 3 and ASC₇₀₀₋₁, 2, 3 present visible stratification. For the solutions of ASC₈₀₀₋₁, 2, 3 and ASC₉₀₀₋₁, 2, 3, although there is obvious liquid-solid stratification, the upper layer solution presents a brown suspension state. This

might be due to the settling related to particle size difference. High temperature (i.e. 800 and 900 °C) calcination results in the presence of ultra-fine particles in the calcined clay. As shown in Table 4-3, the specific surface area of calcined clay increases with the increase of calcined temperature. The agglomeration of metakaolin in calcined kaolinitic clay will affect the hardened properties of calcined clay blended cement based mortar and concrete (Paiva et al., 2012). This suggests that the agglomeration phenomenon of the calcined material could be reduced by dissolving in water. In the future work, the influence of pre-dissolution of calcined kaolinitic materials on physical properties of mortar and concrete should be explored.

Table 4-3 Effect of thermal activations on morphological properties of the SC, i.e. specific surface area (BET) and PSD.

Materials	SC	ASC ₆₀₀₋₁	ASC ₆₀₀₋₂	ASC ₆₀₀₋₃	ASC ₇₀₀₋₁	ASC ₈₀₀₋₁	ASC ₉₀₀₋₁
Specific surface (m ² /g)	5.97	2.93	3.49	4.57	4.56	8.40	10.20
D _{v,50} (µm)	51.75	18.81	18.57	18.33	18.41	18.09	18.92

4.3.2.3 TG-DTG analysis

Figure 4-5 displays the mass change and calculated dehydroxylation ratio of ASCs after different calcination temperatures and time. As shown in Figure 4-5 (a), the mass change of ASCs is less than that of SC. This is due to the water release and dehydroxylation of gibbsite and kaolin in the SC during thermal activation process. When the calcination temperature reaches 600 °C, the mass change of ASC₆₀₀₋₁, ASC₆₀₀₋₂ and ASC₆₀₀₋₃ still show a large change with the extension of the calcination time. This suggests that when calcined at 600 °C for 1 hour or 2 hours, there are still part of kaolin in ASCs that have not undergone dehydroxylation. This may be due to the presence of inter- and inner-hydroxyl groups (as shown in Figure 4-2), which means that the inter-hydroxyl group calcined at 600 °C cannot obtain a good dehydroxylation ratio. However, once the calcination temperature reaches or exceeds 700 °C, the effect of calcination temperature and time on the mass change of ASCs is lower than 1 wt. %.

The calculated dehydroxylation ratios of ASCs after calcination at 600, 700, 800 and 900 °C for 1, 2 and 3 h are shown in Figure 4-5(b). The dehydroxylation ratio of ASC₆₀₀₋₁, ASC₆₀₀₋₂ and ASC₆₀₀₋₃ are 31.2%, 68.3% and 82.3%, respectively. When

the calcination temperature reaches or exceeds 700 °C, the dehydroxylation ratio exceeds 90%. The highest dehydroxylation rate happens at 800 °C for 3 hours, reaching 95.5%. When the calcination temperature increases to 900 °C, the dehydroxylation rate of ASCs slightly increases first and then decreases with the extension of calcination time. The small change in the dehydroxylation ratio might be related to the uneven kaolin content in the SC, or the recrystallization of amorphous phase into mullite due to longer calcination time (over two hours).

In view of the above results, when the calcination temperature is chosen as 700 °C, 800 °C, or 900 °C, 1 hour calcination is sufficient to get the optimal dehydration rate in terms of energy saving. Hence, the following samples are selected for further investigation: ASC₆₀₀₋₁, ASC₆₀₀₋₂, ASC₆₀₀₋₃, ASC₇₀₀₋₁, ASC₈₀₀₋₁ and ASC₉₀₀₋₁.



Figure 4-5. (a) TGA of SC after thermal treatment through different calcination parameters: 600 °C-1h, 2h, 3h; 700 °C-1h, 2h, 3h; 800 °C-1h, 2h, 3h; 900 °C-1h, 2h, 3h; (b) dehydroxylation ratio of ASCs.

4.3.2.4 XRD analysis

To better understand the phase transformation in the process of the thermal activation at different conditions, XRD analyses were carried out and the results are shown in Figure 4-6. For SC, the XRD pattern shows clearly that the crystal phase characteristic peaks of kaolin mainly appear in the range of angles $12 - 40^{\circ} 2\theta$ (Avet et al., 2018), and kaolin and quartz are the dominant composition, with small amounts of gibbsite, muscovite and hematite.



Figure 4-6. XRD patterns of SC and ASCs. The identified minerals are, K: kaolinite, Q: quartz, G: Gibbsite, M: Muscovite, H: Hematite, C: Calcite, I: Illite.

After calcination at 600 °C, the peak intensities of kaolinite in ASCs gradually decreases with prolonged heating time, which indicates that the dehydroxylation ratio of kaolinite to metakaolin increases with prolonged calcination time. The characteristic peaks of kaolin could still be found in sample ASC_{600-3} , indicating the presence of a certain degree of crystallinity. The dehydroxylation ratio obtained by TGA-DTG analysis is consistent with the changes in phase crystallinity obtained by XRD. For ASC_{700-1} , all the characteristic peaks belonging to kaolin have disappeared, which indicates that the crystallinity of kaolinite in ASCs is significantly reduced. There is no new crystalline appearing in samples ASC_{800-1} and ASC_{900-1} , which suggests that the amorphous metakaolin will not recrystallize. The characteristic peaks of quartz at 20.96° and 26.7° 20 remain unchanged, indicating quartz is inert

during thermal activation. Aforementioned results show that when the calcination temperature reaches or over 700 °C, the phase transformation ratio for 1 hour is higher than transformation rate at 600 °C for 3 hours, which is consistent with previous TGA-DTG results.

4.3.2.5 FTIR analysis

Figure 4-7 shows the FTIR spectrums of SC and ASCs treated with different calcination parameters. In SC, three well-defined bands in the range of 3700-3600 cm⁻¹ are defined as stretching vibrations of hydroxyl groups (-OH) (Figure 4-7 a-1) (Alujas et al., 2015). The hydroxyl groups could help to quantitatively and qualitatively analysis the order degree of kaolinite structure in ASCs. Especially the - OH group stretching vibrations at 3694 and 3618 cm⁻¹ is a typical manifestation for well-ordered kaolinite (Fitos et al., 2015). The well-defined band at 3618 cm⁻¹ presents the inner-hydroxyl group which is located at the interface between the Si tetrahedral and the Al octahedral layers, while bands near 3694 cm⁻¹ and 3647 cm⁻¹ (in Figure 4-7 a-2) are the inter-hydroxyl groups originate from the internal Al octahedral surface hydroxyl groups (Madejova and Komadel, 2001, Madejova, 2003). The existence of doublet characteristic peaks at 936 and 912 cm⁻¹ are defined as Al-OH bending vibration bands, which could also be assigned to the proof of the ordered structure of kaolinite (Bich et al., 2009).



(a-1)



Figure 4-7. FTIR spectra of SC and ASCs with different thermal treatment parameters: (a-1,2) 600°C - 1h, 2h, 3h; (b-1,2) 600°C, 700°C, 800°C, 900°C - 1h.

When subjected to thermal activation, the degree of kaolinite structure order decreases, and the band intensities of -OH groups in ASC₆₀₀₋₁ at 3694, 3647 and 3618 cm⁻¹ (in Figure 4-7 a-1) tend to weaken and eventually disappear at ASC₆₀₀₋₂ and ASC₆₀₀₋₃, which consistent with the dehydration phenomenon of the kaolinite during thermal activation. The Al-OH bending vibration bands at 936 and 912 cm⁻¹ in ASC₆₀₀₋₂ and ASC₆₀₀₋₃ (in Figure 4-7 a-2) might merge into the new spectral band in the range of 1200-900 cm⁻¹, which is typical stretching vibrations of Si-O-T band, where T = Si or Al (Wan et al., 2017). As shown in Figure 4-7 b-2, there is a peak shifting (around 54 cm⁻¹) of the main band at 1200-900 cm⁻¹ in FTIR spectra of ASC₇₀₀₋₁, ASC₈₀₀₋₁ and ASC₉₀₀₋₁ compared with the ASC₆₀₀₋₃, which indicates the increase of Si/Al ratio in the group. The stretching vibrations band of Si-O at 1115 cm⁻¹ is assigned as the vibration of apical oxygen atoms perpendicular to kaolin structure layer, which is mightily influenced and appears the loss of delamination stacking sequence between layers (Aglietti et al., 1986).

During calcination, the kaolinite emerges different degrees of collapse and transformed to metakaolin, which could be proofed by the appearance of new broad bands centred at around 1050 and 450 cm⁻¹ (amorphous Si-O-Al bond stretching) caused by the combination of the bands at 1115 cm⁻¹ (Si-O bond), 1030 cm⁻¹ (Si-O-Si bond), 1001 cm⁻¹ (Si-O-Al bond), 936, 912 cm⁻¹ (Al-OH bonds), and the bands at 528 cm⁻¹ (crystallized Si-O-Al bond) and 460, 419 cm⁻¹ (Si-O bond), respectively (Ilić et al., 2010, Souri et al., 2015).

4.3.2.6 . NMR analysis

The effect of thermal activation on the kaolinite and metakaolin structures in SC and ASCs are also investigated by ²⁷Al and ²⁹Si NMR, as shown in Figure 4-8, where the different coordination sites of Al and Si could be clearly distinguished.

In Figure 4-8(a), the main peak showed at around -6.0 ppm for SC and ASC₆₀₀₋₁ is assigned to six coordination aluminium (Al^{VI-1}), which indicates a well ordered Al-O octahedral structure in materials (Fernandez et al., 2011, Liu et al., 2001). When the calcination temperature rises to 700 °C, the main peak shifted to 0 ppm (Al^{VI-2}), which might due to the decrease of bond angle (θ_{AI-O-T}) or bond length (d_{AI-O-T}) in the Al-O octahedral (Edén, 2015). Two new peaks locating at 29 and 56 ppm are

identified, which are attributed to the formation of five and four coordination of aluminium (Al^V and Al^{IV}) in Al-O hexahedron and tetrahedron, respectively. The presence of new resonances and the breadth of the resonances in ASC₈₀₀₋₁ suggest that the Al within the ASCs with a disordered structure and implies a breakdown of the original crystalline structure in SC after thermal activation. As the temperature gradually increases to 900 °C, the resonance peaks gradually sharpen, especially Al^{V-2}, which indicates the formation of poorly ordered Al^V environments in ASC₉₀₀₋₁. Simultaneously, Al^{V-1} shifts to the left and forms a new characteristic peak Al^{V-2}, and the dominant coordination are Al^{IV} and Al^{V-1}, as shown in Figure 4-9(a).

The change of Al coordination is related to the dehydroxylation of kaolinite after calcination. As the temperature increasing, the intensity of the Al^{IV} and Al^V peaks gradually increases, while the intensity of the Al^{VI} shows a relatively weakening trend. The remaining Al^{VI} in ASC₈₀₀₋₁ and ASC₉₀₀₋₁ is attributed to the crystallinity impurities (such as muscovite) in ASCs.

In Figure 4-8b, the ²⁹Si NMR spectra of SC and ASCs are present and probed the structure environment around silicon atoms in materials, where, n and m in Qⁿ (mAl) represent the number of bridged oxygen atoms in Si sites and the number of bridged Al atoms, respectively (Ferone et al., 2015).

The SC sample shows two single peaks with good symmetry at around -93 and -109 ppm, indicating two crystalline Si states, i.e. Q^3 (2Al) in kaolin and Q^4 (0Al) in quartz, respectively. For ASC₆₀₀₋₁, the new peak at -102 ppm is identified, indicating the presence of Q^3 (1Al), which is related to the dealumination of Si-O-Al bond during activation process and consistent with FTIR results. As the temperature increases to 700 and 800 °C, the peak intensity of Q^4 (0Al) at -109 ppm increases while that of Q^3 (2Al) becoming weaken and forming an asymmetric broad peak band. When the temperature reaches to 900 °C, the peak at -93 ppm almost disappears, and there is only one main characteristic peak at -109 ppm, which is the characteristic chemical shift of Q^4 in tetrahedral (Liu et al., 2001).



Figure 4-8. ²⁷Al (a) and ²⁹Si (b) NMR spectra of SC and ASCs.





Figure 4-9. ²⁷Al and ²⁹Si MAS NMR data (black line), simulation (red line) and spectral deconvolutions for ASC_{900-1} . Alⁿ and Q⁴ (mAl) assignments are made with the reference as noted in (Longhi et al., 2019, Walkley and Provis, 2019).

Although there is only one characteristic peak located at -109 ppm in ASC₉₀₀₋₁, the peak is not completely symmetrical on both sides, and the intensity on the left is significantly higher than that on the right. After deconvolution for ASC₉₀₀₋₁ curve (as shown in Figure 4-9 b), there is still a small amount of Q³ (2Al) or Q³ (1Al), which might be explained by the Equation 4-8 (Wei et al., 2005). As can be seen from the equation that the Si-O-Al bond in metakaolin will break from around 850 °C and gradually release amorphous reactive SiO₂. It is notable that this chemical reaction will increase the pozzolanic reactivity of ASCs by changing the Al and Si coordination (Hollanders et al., 2016, Garg and Skibsted, 2016, Alujas et al., 2015). These changes cannot be observed by TGA, XRD results.

$$Al_2O_3 \cdot 2SiO_2 \xrightarrow{\sim 850 \, \mathcal{C}} xSiO_2 + Al_2O_3 \cdot (2 - x)SiO_2$$
Equation 4-8

4.3.3 Mortar compressive strength

Figure 4-10 shows the compressive strength and strength activity index of mortars with 30% replacement of cement by ASCs at 7 days and 28 days. Two control groups, OPC based mortar (M_{OPC}) and 30% SC replacement of cement-based mortar (M_{SC}) are applied as references. The SAI of M_{OPC} is set as 100%. According to the standard ASTM C 618, when the SAI of samples exceeds 75% of OPC, the material is assigned as potential pozzolanic materials and can be used as SCM. It is interesting to find that the SAI of all ASCs and M_{SC} exceeds 75% of M_{OPC} ,

indicating the high potential pozzolanic reactivity of ASCs. Moreover, the compressive strength of ASCs blended cement-based mortar exhibits comparable or even higher value than that of M_{OPC} . Increasing the curing age to 28 days, the SAI of all ASCs exceed 75%. The compressive strength of all mortar samples increases, and M_{900-1} shows the highest improvement, which is 26.9%.

In view of the above results, ASCs obtained at higher calcination temperature shows higher compressive strength in mortars. It seems that the superior performance of ASCs as SCMs is not only related to the pozzolanic reactivity brought by the dehydroxylation and coordination changes of kaolinite, but also affected by the filler effect of unreacted metakaolin and inert micro-quartz, which improves the pore structure of mortars and further increases the compressive strength. It can be inferred from the SAI data that the increase of compressive strength is contributed to the coupling effect of metakaolin pozzolanic reaction and filler effect at 7 days. However, at 28 days, the pozzolanic reaction of metakaolin in SC plays the dominant role in the compressive strength. This is inferred from the negative effect of SC in the compressive strength of M_{SC} at 28 days.





Figure 4-10. SAI (as shown in column) and compressive strength (as shown in curves) of ASCs blended cement-based mortar after (a) 7 days and (b) 28 days curing at 20 ± 2 °C.

4.3.4 Pozzolanic reactivity assessment

4.3.4.1 IC test and analysis

The heat release rate and cumulative heat release for 30% ASCs-OPC blends and OPC paste are shown in Figure 4-11(a) and (b), respectively. There are four exothermic peaks appeared for all mixtures as shown in Figure 4-11(a). The first exothermic peak is related to the initial wetting and dissolution of raw materials (Yao et al., 2009). It is found that ASCs substitution has no significant effect on the first exothermic peak and the onset time of the four exothermic peaks. The replacement of OPC by ASCs reduces the intensity of exothermic peaks II and III, which are corresponded to the hydration of C₃S and C₃A, respectively (Zunino and Scrivener, 2021, Quennoz and Scrivener, 2013). It could be found that ASCs promotes the C₃A hydration more than C₃S hydration (Du and Dai Pang, 2018). Rossen et al. explained that this might be due to the fact that replacing OPC by SCM reduces the amount of gypsum available in the system, resulting under-sulfation, in which case the third peak is significantly higher (Rossen et al., 2015). In terms of the shoulder peak IV in OPC paste, this is the conversion process of AFt to AFm. However, in ASCs-OPC blends paste, peak IV basically disappeared.

The hydration of C_2S and C_3S in OPC mainly occurred at the first 20 hours and formed C-S-H gel and calcium hydroxide. Hence, there is minor difference among

cumulative release heat in the ASCs-OPC blends at the first 20 hours as shown in Figure 4-11(b). The deviation of the cumulative release heat of ASCs-OPC blends occurs because of the different pozzolanic reactivity of ASCs. The metakaolin in ASCs reacts with calcium hydroxide forms the calcium aluminium substituted silicate hydrate (C-(A)-S-H). It is found that the ASCs could reduce the cumulative release heat in blends by 15%-20%, as shown in Figure 4-11(b). The heat reduction gradually decreases with the extension of calcination time and increase of calcination temperature. This is due to the difference in the content of metakaolin and the difference in ²⁷Al and ²⁹Si coordination. IC test method is an effective method to evaluate the pozzolanic reactivity of activated kaolinitic clay or other pozzolans.



Figure 4-11. Heat release rate (a) and cumulative heat release (b) normalized for per gram of OPC and ASCs-OPC blends at 25 °C.

4.3.4.2 LC test and analysis

The lime consumption results are shown in Figure 4-12. The remaining amount of calcium hydroxide and calcium carbonate in portlandite and ASCs pastes were measured by TGA-DTG test, as shown in Figure 4-12-a. There are three stages of mass change: stage I from around 50-420 °C caused by bond water release from C-(A)-S-H (magnified in Figure 4-12 a-2, b-2) (Avet et al., 2016, Collier, 2016), stage II from around 425-500 °C caused by calcium hydroxide decomposition, stage III from around 560-730 °C caused by calcium carbonate decomposition (Collier, 2016).





Figure 4-12. TGA curves of lime-ASCs pastes: (a) TGA curves of 7d cured pastes; (b) TGA curves of 28d cured pastes.



Figure 4-13. Lime consumption ratio in lime-ASCs pastes with different curing ages: (a) 3 days curing (b) 7 days curing (c) 28 days curing.

According to the Equation 4-6 and Equation 4-7, the lime consumption ratio of the mixtures are shown in Figure 4-13. The consumption ratio of lime significantly increases with the increase of calcined temperature, which is due to the increase of the pozzolanic reactivity of ASCs. After 3 days, the lime consumption ratio of ASC₉₀₀₋₁ is higher than all ASC₆₀₀, and the consumption ratio of ASC₈₀₀₋₁ is similar. Compared with 3 days curing, the consumption ratio at 7 days has minor change, and the highest growth ratio belongs to ASC₆₀₀₋₁ (around 33.5%), and the smallest is ASC₉₀₀₋₁ (around 5.2%). Increasing the curing ages to 28 days, it can be found that the lime consumption of different ASCs is significantly different, and ASC₈₀₀₋₁ and ASC₈₀₀₋₁ exhibits superior pozzolanic reactivity. The reason is related to the different dehydroxylation ratios and the changes of silicon and aluminium coordination, as discussed in TGA-DTG and NMR analysis.

The products of pozzolanic reaction in lime-ASCs system are calcium silicate hydrate (C-S-H) and C-(A)-S-H (Tironi et al., 2013), and the bond water decomposition temperature is between 50 and 425 °C, which is the stage I as shown in Figure 4-12(b). The bond water determination is another method to evaluate the pozzolan reactivity of ASCs by calculating the product content of the pozzolanic reaction (Avet et al., 2016). The bond water content is shown in Figure 4-14. The released mass of bond water illustrates that the reaction degree after curing to 3 and 7 days is about 38% and 56% of 28 days, respectively. With the increase of curing age, the change in the quantity of reaction products and the consumption of lime have a more consistent trend. Due to insufficient metakaolin content, the bond water content of ASC₆₀₀₋₁-lime and ASC₆₀₀₋₂-lime mixtures at 28 days is much lower than that containing ASC₇₀₀₋₁, ASC₈₀₀₋₁, ASC₉₀₀₋₁ and ASC₉₀₀₋₁ possess higher pozzolanic reactivity than others.



Figure 4-14. Bond water released from C-(A)-S-H formed in lime-ASCs pastes after different curing ages.

4.4 Conclusions

The waste kaolinitic sandstone clay produced from sand manufacturing contains about 50% of kaolinite. It is confirmed that SC can be used as SCM after thermal activation. Compared with other low-grade kaolinitic by-products, the SC has a greater advantage in fineness and can eliminate the mechanical grinding process.

As demonstrated by FTIR and NMR data, the pozzolanic reactivity of the calcined clay is derived not only from the kaolinite dehydroxylation reaction, but also from the alternating of the ²⁷Al and ²⁹Si coordination environments generated by Si-O-Al bonds breaking. The calcination temperature and time are the dominant factors affecting the pozzolan reactivity of ASCs. When the calcination temperature is 600 °C, the calcination time needs at least 3 hours, and prolonging heating time can increase the dehydroxylation ratio. When it rises to 700-900 °C, 1 hour of calcination is sufficient to obtain high pozzolanic reactivity.

When ASC is used as SCM in paste or mortar, besides the higher pozzolanic reactivity, it also illustrates significant filler effect due to the existing of micro-quartz, which contributes to the compressive strength development in the early stage. The compressive strength of OPC-ASC based mortar is comparable, or even, better than that of OPC based mortar, but the hydration heat is lower. In specific, the

compressive strengths of ASC₇₀₀₋₁, ASC₈₀₀₋₁, and ASC₉₀₀₋₁ blended mortars are 7%, 10% and 16% higher than the OPC based mortar. SC activated at high temperatures outperformed other low-grade clays, demonstrating the performance of high quality SCMs. Finally, based on this comparison of different approaches, it is recommended to use TGA-DTG technique to evaluate the pozzolanic reactivity of ASC as this method is very efficient in determining calcium hydroxide consumption capacity by measuring the calcium hydroxide content and the bond water content of the hydration products.

CHAPTER 5. PHASE EVOLUTION AND MICROSTRUCTURE DEVELOPMENT OF LC³ AT MODERATE TEMPERATURES (100 - 400 °C)

Note: The content of Chapter 5 is based on the manuscript entitled "**Thermal stability of** *limestone calcined clay cement (LC³) at moderate temperatures 100 - 400 °C*", by Yubin Cao, Yanru Wang, Zuhua Zhang, Yuwei Ma and Hao Wang, published in the journal of *Cement and Concrete Composites*, 2022.

5.1 Introduction

The annual greenhouse gas (CO₂) emissions produced from PC production are approximately 8% of the global CO₂ emissions generated by human activities (Miller et al., 2018). One of the effective approaches for minimising the CO₂ footprint caused by cement manufacturing on a worldwide level is to lower the clinker proportion by increasing the fraction of low-CO₂ supplementary cementitious materials (SCMs) (Environment et al., 2018). At present, the output of commonly used SCMs such as ground granulated blast furnace slag (GGBS) and fly ash accounts for around 15% of the cement output (Briki et al., 2021). However, with the application of cleaner fuels in power plants, the supply of fly ash is expected to decrease (Environment et al., 2018). Hence, it is vital to broaden the sources of low-CO₂ SCM resources, such as limestone powder and calcined clay.

Limestone calcined clay cement (LC³), coupling of limestone and low-grade calcined kaolinitic clay to replace clinker, shows great potential as a viable alternative to PC (Scrivener et al., 2018b). The feasibility is attributed to the fact that kaolinitic clay and limestone are two widely distributed materials, which solve the issue of insufficient storage and uneven distribution of traditional SCMs. On the other hand, due to the pozzolanic reactivity of calcined clay and the synergistic reaction of limestone and calcined clay, the substitution level of clinker in LC³ can reach as high as 50 wt. %, and the hardened product exhibits comparable compressive strength to PC after 7 days (Avet et al., 2016). Wang et al. (2021) studied the use of LC³ to produce high-strength cement based composites (Wang et al., 2021a). By using limestone and calcined clay to replace 10%, 30% and 50% of

cement, the compressive strengths reached 147, 142 and 124 MPa, respectively, after 28 days of curing. For the microstructure, Dhandapani and Santhanam (Dhandapani and Santhanam, 2020) found that the additional compounds in the LC^3 system e.g. C-A-S-H and CO₃-AFm phases, can significantly modify LC^3 transport property and achieve higher tortuosity at early stage, which means low permeability from the early age. Avet and Scrivener (2018) also reported that coupling replacement of clinker by limestone and calcined clay had little effect on the total porosity, but it can refine the pore structure and reduce pore connectivity (Avet and Scrivener, 2018b). Hence, LC^3 based mortar and concrete have demonstrated superb mechanical property and long-term durability.

Owing to these advantages of inorganic cement material, such as high temperature resistance, global distribution, and competitive prices, it can be utilized in variety of applications, including vapor collector, radioactive wastes and solid-state thermal energy storage (Laing et al., 2006, John et al., 2013, Suescum-Morales et al., 2021). However, in these applications, the cement products will be subjected to perennial moderate temperatures in the range of 100 - 300 °C (Oró et al., 2012). In addition, with the development of power generation in the nuclear industry, the annual production of radioactive wastes is increasing. Concrete is usually used for temporary storage and long-term management of the wastes, which means the cement matrixes need to be exposed to moderate temperatures (50-200 °C) over considerable periods (Farage et al., 2003). Previous studies (Heikal, 2000, Ma et al., 2015) found that the residual compressive strength of PC products kept constant or slightly increased from ambient to 300 °C, although overall porosity increased, and surface damage was observed. Lin et al. (2021) also found similar results in LC^3 paste after exposing to 300 °C for 2 hours. Most researchers recognize that when the temperature rises from ambient to 300 °C, evaporable water (e.g. free water, interlayer water and surface adsorbed water) of PC paste will be released, and different calcium aluminate hydrate phases will be dehydrated, while over 350-400 °C, calcium hydroxide decomposes to form calcium oxide, at which stage the residual strength will drop sharply (Collier, 2016, Abid et al., 2017).

Previous research on PC related to the effect of temperature mainly focused on the refractory performance or high temperature resistance (Lin et al., 2021), and the

exposure duration is relatively short in the range 1-3 hours, where the test conditions may vary. The damage generated to the microstructure by thermal treatment might be partially recovered or changed with ageing. There are rare studies on the microstructure development and phase evolution of heated cement products at moderate temperature (below 400 °C) for a longer duration nor rehydration properties after exposed to higher temperature. LC³ based products usually have more C-A-S-H, AFt and CO₃-AFm phase than PC. However, the difference in microstructure development and phase evolution of PC and LC³ under the specific moderate temperature treatment is not clear.

To better understand the physical behaviours of PC and LC³ products at moderate temperatures (≤ 400 °C) over long-term exposure, the research on their phase evolution and microstructure development is needed. This study was conducted from four aspects: (i) the impact of moderate thermal treatments on the mechanical properties of PC and LC³ products, (ii) the influence of moderate temperatures on the evaporation of free water, interlayer adsorbed water and chemically bounded water, (iii) the influence of moderate temperatures on the open porosity and, (iv) the effect of moderate temperatures on the evolution of hydration phases. After thermal treatments, the length, cracks and density of cement products were characterised. The impact on residual compressive strength and microstructure development were also investigated. Thermogravimetric analysis (TGA), scanning electron microscopy (SEM), Fourier transformed infrared (FTIR) and X-ray diffraction (XRD) were conducted to analyse the phase evolution. ²⁷Al and ²⁹Si NMR spectra and deconvolution analyses were used to identify the chemical coordination and mean chain length changes.

5.2 Experimental procedures

5.2.1 Materials and mixture design

The PC used in this research was supplied by Cement Australia, a product as per Australia Standard AS3972. The waste clay was supplied by Rock Trade Industry - Waterfall Quarry (Queensland, Australia), which was sourced as a by-product from sandstone artificial sand manufacturing. The chemical compositions are shown in Table 5-1, which were measured by X-ray fluorescence (XRF).

The calcined clay (CC) with around 50 wt. % of metakaolin was obtained by burning waste clay at 800 °C for 1 hour. Details can be found in (Cao et al., 2021b). Limestone powder (LS) was supplied by ChemSupply Australia Pty Ltd, in which calcium carbonate content was over 98% and specific gravity was around 2.7-2.95 g/cm³. The particle size distribution (PSD) of the starting materials, as calculated by laser diffraction using Malvern Mastersizer, is presented in Figure 5-1. The mean particle size distribution (D_{v50}) of PC and CC were 20 and 12µm, respectively. Polycarboxylic superplasticizer was utilized to improve the workability of fresh mortar.

Table 5-1 Chemical compositions of materials as measured by XRF, wt%.

Materials	Constituent (wt. %)										
	SiO ₂	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na ₂ O	K ₂ O	TiO ₂	MnO	Others
PC	20.24	5.15	3.17	65.13	1.33	3.41	0.44	0.52	0.28	0.08	0.25
LS	0.09	0.00	0.02	54.97	0.09	0.03	0.05	0.00	0.00	0.00	42.6
CC	66.09	29.31	2.65	0.04	0.15	0.02	0.04	0.53	0.83	0.04	0.32
Gypsum	1.39	0.17	0.08	41.2	1.06	55.7	0.00	0.07	0.00	0.00	0.33



Figure 5-1. Particle size distributions of PC and CC.

There were two series of mixtures in this study, mortar (abbreviated as M) for macro property study and paste (abbreviated as P) for microstructure study. The detailed mixture proportions for the LC^3 and PC are shown in Table 5-2. The cement replacement level in LC^3 was around 47 wt. %, and 2 wt. % content of anhydrite by cement was blended in LC^3 (Zunino and Scrivener, 2021). The water to binder (w/b) ratio and sand to binder (s/b) ratio of mortar were 0.475 and 2.5, respectively. The

w/b ratio of paste was 0.325. Since the dominant component in CC is metakaolin, which has higher water absorption property, polycarboxylic superplasticizer is needed to improve the workability of LC^3 paste and mortar to achieve targeted flowability.

Mix No.	PC (wt. %)	CC (wt. %)	LS (w	t. Gypsum (wt. %)	Water reducer (wt. %)	Flowability (cm)
M _{PC}	100	-	-	-	-	21.4
M _{LC3}	53	30	15	2	0.2	21.1
P _{PC}	100	-	-	-	-	-
P _{LC3}	53	30	15	2	0.3	-

Table 5-2 Mixture designs of PC and LC³ pastes and mortars (wt. %).

5.2.2 Sample preparation and heating regimes

The dry materials were firstly mixed for 2 mins with a mechanical stirrer. Followed by this, water was added and then stirred at 285 rpm/min for 5 mins. The fresh mortars and pastes were cast into cubic and prismatic moulds with a size of $40 \times 40 \times 40$ mm and $20 \times 20 \times 80$ mm, respectively. After 24 h ambient curing, the samples were demoulded and sealed with a plastic film to avoid the loss of moisture and carbonation. The samples were subsequently put in a curing room at 20 ± 2 °C until 150 days.

The cured samples were thermally treated from ambient temperature to 100, 200, 300 and 400 °C in an electric muffle furnace, respectively, and held at the target temperature for 6 hours. The heating rate was 10 °C/min. After reaching 80% of the target temperature, the heating rate was changed to 5 °C/min to avoid overshooting due to the fast-heating rate. After the heating program was completed, the furnace was programmed to cool down to room temperature at a cooling rate of 5 °C/min. This slow cooling process can avoid thermal shock cracks which could occur at a rapid cooling rate.

5.2.3 Test methods

5.2.3.1 Length change and visual inspection

The length change of each side of the mortar mixture before and after exposure to thermal treatment was measured with a Vernier calliper three times and the average value was reported. The mass change of each mortar mixture was taken as the average from three samples. The volume change and bulk density of each mortar mixture were then calculated from the above results. The surface change of the mortar and paste samples was recorded by an optical microscope.

5.2.3.2 Mechanical properties

The residual compressive strength of the LC³ and PC mortars sample before and after moderate temperature exposure was tested by an MTS universal mechanical testing equipment with a loading speed of 1 mm/min. Moisture loss and decomposition of the hydration products will influence the brittleness of the sample, which is generally used to describe the tendency of structures to fail unexpectedly before causing serious irreparable damage. To better understand how the brittleness of the sample changes after moderate temperature treatments, the brittleness index (BI) was calculated as follows (Farzadnia et al., 2013):

 $BI = (Elastic \, energy) / (Total \, energy)$ Equation 5-1

Elastic energy and total energy were determined by the area under the branch of rising compressive stress and the total area under the curve of compressive stress, respectively.

5.2.3.3 Water absorption test

Besides air, water is the primary medium for transporting hazardous ions (e.g., Cl⁻, H⁺, SO₄²⁻) to the interior of cementitious matrices under the action of capillary pressure (Zhang et al., 2021). Water absorption amount and rate is considered to be promising indicators for assessing the open porosity and pore connectivity of mortars (Wang et al., 2019b). To understand the microstructure damage induced by different moderate temperatures to the hardened matrix, water absorption test was performed. Due to the uneven distribution of cracks after heating program, the paste samples (20 \times 20 \times 80 mm) were completely immersed in distilled water (liquid-solid ratio was 10:3) to test the water absorption performance. This experiment was carried out in a sealed plastic container to avoid carbonation and water evaporation. The pH value of the solutions was measured and recorded at the same time.

Before the water absorption test, the mass (m_{dry}) of the calcined samples were measured and recorded. To evaluate the effect of different calcination temperatures on the open porosity, the water-saturated samples (m_{sat}) were dried at 50 °C oven

until obtaining constant weight ($m_{50^{\circ}C}$). The (re)hydration performance of samples after moderate temperature treatment was calculated according to Equation 5-2. Total open porosity (\emptyset) was provided as a function of the water loss mass as per Equation 5-3, and the mass loss of water was according to saturation and drying processes ($\Delta m = (m_{sat} - m_{dry})$).

 $M_{(re)hydration} = m_{50^{\circ}\text{C}} - m_{dry}$ Equation 5-2

$$\phi = \frac{m_{sat} - m_{dry}}{V \cdot \rho_w}$$
Equation 5-3

where, m_{sat} and m_{dry} are the mass of the thermally treated samples after water saturation and the mass of the samples heated at same temperature (g); $m_{50^{\circ}C}$ is the mass of saturated samples after 50 °C oven drying (g); Ø is the open porosity (%); V represents the volume of samples (m³); and ρ_w is the density of distilled water at room temperature at 20 °C (998.21 kg/m³).

5.2.3.4 Micro characterisation

Part of the paste samples were cut and reserved the original fracture surface for scanning electron microscopy (SEM) tests. Others characterization test, such as TGA-DTG, FTIR, XRD, and MAS NMR, were conducted with ground paste powders.

TGA-DTG test was performed using a Discovery SDT 650 from TA Instruments. Under nitrogen atmosphere, the PC and LC³ paste powders were heated from ambient temperature to 1000 °C at a speed of 10 °C/min. To further study the influence of the moderate temperatures (100, 200, 300 and 400 °C) on the evaporation of chemically bond water from PC and LC³ pastes, the samples were isothermally treated for 2 hours, when the program rose to the target temperature. The mass losses at the ascending stage and isothermal stage were recorded.

SEM test was conducted with a Hitachi SU3500. The LC^3 samples were gold-coated by a JEOL smart coater prior to testing. The internal damage and hydration product changes were observed at different magnifications at 10 kV.

FTIR test was performed utilizing a PerkinElmer FTIR spectrometer in a wavelength range between 4000 to 400 cm^{-1} to identify the changes in the

characteristic bands of hydration products in LC^3 and PC paste powders before and after exposure to different thermal treatments.

XRD patterns of the PC and LC³ paste powders were collected from 5 to 65° 2 θ , with 0.01° 2 θ step size. Cu K α radiation was used with a wavelength of 1.54 Å, a voltage 40 kV, and current 40 mA. The collected diffraction patterns were treated and identified by Jade 6 including powder diffraction file (PDF) database.

MAS NMR test was conducted to evaluate the Si and Al coordination environments and Si/Al ratio variations of LC^3 and PC pastes after different moderate temperature treatments. A Bruker 300 MHz Avance III 400 WB spectrometer with double air bearing 4 mm MAS probe was utilized to collect the spectra. The powder was spined at 8 kHz with 1 µs pulse (pi/12) and 1 s relaxation interval. CPMAS spectra were used to confirm the position of coordination characteristic peaks. The peak deconvolution was performed with Gaussian in Origin software.

5.3 **Results and discussion**

5.3.1 Length change and visual inspection

Under different moderate temperatures, due to the physical and chemical influences, cement products will undergo volumetric changes and density changes with the generation of cracks (Yüzer et al., 2004). Figure 5-2 shows the length and density changes of the mortars and the cracks development of pastes after different moderate temperature treatments.

Figure 5-2 (a) shows the length change of PC and LC³ mortars. The length change is the result of the coupled effects of crack expansion and drying shrinkage (Ba et al., 2013, Hager, 2013). As the temperature increases from ambient to 400 °C, the length of the PC and LC³ mortars first decreases at 100 °C and then increases from 200 °C. When the temperature rises from ambient to 100 °C and 200 °C, the free water and part of the chemically bonded water evaporate, causing the samples to shrink as it dries and dehydrates. At this stage, no obvious cracks were observed at 100 °C and fewer cracks are found at 200 °C, as shown in Figure 5-2 (c).

As the thermally treated temperature rises to 300 and 400 °C, the samples undergo thermal expansion and contraction during the heating and cooling process. Due to

the different thermal expansion coefficients of different phases in the hardened samples, micro and macro cracks form at this stage (Hager, 2013). And as the temperature increases, the damage (the number and width of cracks) of the sample gradually increases, as shown in Figure 5-2 (c). At 400 °C, transverse penetration cracks occur on both PC and LC³ surfaces. When thermally treated at 100-300 °C, the length change of the PC sample is larger than that of the LC³ sample, and more cracks were observed in the PC sample. It is worth noting that compared with the paste sample, the mortar sample shows almost no cracks at 100-300 °C.

Figure 5-2 (b) shows mass and density changes of the PC and LC^3 samples. At 20 °C, the density of LC^3 sample is lower than that of the PC sample. From ambient temperature to 100 °C, the reduction in density is 0.09 and 0.11 g/cm³ for PC and LC^3 samples, respectively. As the temperature increases, the density of PC and LC^3 samples gradually decreases and tends to be constant. In terms of mass change, the main stages occur at 100 °C and 200 °C. And after 100 °C, the mass loss of PC starts to be greater than that of LC^3 , which means LC^3 mortar possesses better thermal resistance to avoid water evaporation after exposed to higher temperatures.





Figure 5-2. (a) Length change ratio of mortar samples, (b) density change of mortar samples and (c) crack development of paste samples after different thermal treatments.

5.3.2 Compressive strength and brittleness index

The residual compressive strength and brittleness index of PC and LC³ mortars after different moderate temperature treatments are shown in Figure 5-3 (a) and (b), respectively. At room temperature, the compressive strength of LC^3 is slightly lower than that of PC. For the residual compressive strength, when subjected to 100 °C for 6 hours, the compressive strength of both PC and LC^3 samples is reduced by 8.5% and 13.1%, respectively. This may be attributed to the evaporation of free water and physically adsorbed water in open pores, which makes the mortar matrix more porous (Eidan et al., 2019, Suescum-Morales et al., 2021). At temperatures of 200 and 300 °C, compared with ambient temperature, the residual compressive strength of PC exhibits a significant improvement, increasing by 14.6% and 15.6% respectively. Previous research (Peng et al., 2001, Rashad and Zeedan, 2012) suggested that the increase is attributed to the hydration between unhydrated cementitious materials and steam. Compared with liquid water, steam has better diffusivity. Furthermore, the steam environment can form the so called "internal autoclave", producing additional hydration products (Saad et al., 1996). Same with those reported by others (Abid et al., 2017), the reduction of compressive strength starts from 400 °C onwards, which is due to the calcium hydroxide (CH) decomposition and the breakage of C-(A)-S-H. At 400 °C, the compressive strength reduction (compared with ambient temperature) of PC and LC^3 is 32.7% and 35.5%, respectively.

The brittleness can indicate the stability of cement products before obviously irreversible deformation develops under stress (Zhang et al., 2002). Figure 5-3 (b) shows the effect of different thermal treatments on the brittleness index as the temperature rises. As one can see that the brittleness index shows a similar trend to the residual compressive strength (Farzadnia et al., 2013). Zhang et al. (2002) suggested that besides calcination temperature, the brittleness index is also related to the heating time and evaporation of gel water.



Figure 5-3. Compressive strength (a) and brittleness index (b) of PC and LC³ mortars after different moderate temperature treatments.

5.3.3 TGA-DTG analysis

5.3.3.1 Mass change analysis

Figure 5-4 shows the TGA-DTG results of PC and LC^3 powder and the influence of heating time at the specific temperature on the mass loss. When the calcination temperature increases from room temperature to 1000 °C, a sequence of complicated physical and chemical transformations occurs in the cementitious material, which leads to mass changes. As shown in Figure 5-4 (a), as the temperature increases, the mass loss is mainly attributed to the free water evaporation, the dehydration of hydration products (e.g. C-(A)-S-H, ettringite-AFt, monosulfate-Ms,

monocarboaluminate-Mc, hemicarboaluminate-Hc and portlandite-CH) and the decomposition of calcium carbonate (Machner et al., 2018a). Compared with block samples, it is much easier for the powder sample to release free water in the open pore, and the evaporation peak of free water is observed at 50-60 °C. C-(A)-S-H is the main strength provider, and its dehydration starts at 60 °C and continues to 400 °C (Collier, 2016). The dehydration of the portlandite process is observed between 400 and 460 °C. It can be seen from the TGA results that the portlandite content in LC³ is lower than that in PC. On the one hand, the replacement of CC and LS reduces the content of cement, thereby reducing the amount of CH produced by cement hydration. On the other hand, the addition of CC and LS consumes portlandite and generates additional C-(A)-S-H, Hc and Mc. Furthermore, the mass change from 600 to 800 °C is attributed to the decomposition of the initially present calcite and later carbonated portlandite. It is observed that carbonated portlandite and limestone have different optimum decomposition temperatures (Shao et al., 2014).

To better explore the effect of isothermal time on mass loss, Figure 5-4 (b) shows the mass change of two-hour isothermal two hours when the temperature reaches the specific temperature. After two hours of isothermal treatment, a certain percentage of mass loss can be observed. At 100 °C isothermal for two hours, the mass changes of LC³ and PC are the largest, 4.5% and 3.9%, respectively. It is worth noting that PC has a larger mass loss of about 4.6% at 400 °C, which is attributed to the portlandite decomposition.

Figure 5-4 (c) shows the total mass loss of PC and LC³ at temperature ascending stage and isothermal stage. The mass loss mainly occurs in the temperature ascending stage at a heating rate of 10 °C /min, but there is still a certain degree of mass loss during isothermal stage, especially at 100 °C and 400 °C. Before 400 °C, the mass loss of LC³ is slightly greater than that of PC due to the evaporation of free and chemically bound water. Different from mass loss of mortar samples (Figure 5-2 c), at 100 °C, the mass loss of LC³ powder is greater than that of PC, which may be attributed to the better microstructure and weaker pore connectivity of LC³ mortar and effectively prevent the evaporation and loss of water.



Figure 5-4. TGA-DTG test of PC and LC³: (a) TGA-DTG curves, (b) mass change during isothermal 120 min, (c) total mass change during ascending stage and isothermal stage.

5.3.3.2 Chemically bond water

For hardened cement samples, the temperature commonly used to dry samples is around 100 °C (Wang et al., 2019a, Avet et al., 2016). This is due to the fact that evaporation of interlayer and adsorbed water need to overcome the solid phase surface adsorption constraint and becomes water vapour at around 100 °C, which gradually escapes the material (Feldman and Ramachandran, 1971). However, drying at 100 °C will cause the decomposition of hydration products, as highlighted in Figure 5-4 (a). The powder is relatively more conducive to water evaporation. Hence, in order to accurately test the effect of calcination temperature on the escape of chemically bound water, low temperature of 50 °C was used to evaporate the free water. The mass loss of bond water (ML_{BW}) is calculated using the following equation:

$$ML_{BW} = ML_{t-a} + ML_{t-i2h} - ML_{50-i3h}$$
 Equation 5-4

where, ML_{t-a} is the mass loss in the ascending stage at specific temperature; ML_{t-i2h} is the mass loss of isothermal at specific temperature for 2 hours, and ML_{50-i3h} is the mass loss of isothermal at 50 °C for 3 hours. Figure 5-5 shows the chemically bound water derived after 2 hours isothermal at specific temperature. At 100 °C, the content of chemically bound water in LC^3 is similar to PC, which is attributed to the free water evaporation, the decomposition of ettringite, AFm phases and the part of dehydration of the C-(A)-S-H. Starting from 200 °C, the chemically bound water content in PC (6.67 wt. %) begins to exceed LC^3 (6.13wt. %). At 300 °C, the difference between the chemically bound water content in PC and LC^3 further increases to 1.01%. Since the content of portlandite in PC is higher than that in LC^3 , hence at 400 °C, 4.10% and 1.79% of bound water are lost in PC and LC^3 , respectively.



Figure 5-5. The loss of chemically bound water from PC and LC³after different thermal treatment.

5.3.4 Water absorption analysis

5.3.4.1 Water absorption and evaporation analysis

Water absorption results (e.g. water absorption amount and rate) can be used as useful indicators to assess the damage caused to cement products after different temperature treatments, such as pore connectivity and open porosity (Farage et al., 2003). Figure 5-6 shows the water absorption of PC and LC^3 pastes for 6 hours period after different moderate temperature treatments. The water absorption rate is mainly affected by the connectivity and porosity of open pores. It can be observed from Figure 5-6 (a) and (c) that the water absorption of the sample mainly occurred in the first 40 hours, especially in the first 3 hours, which is mainly affected by water pressure and capillary pressure (Zhang et al., 2017).

Compared with sample drying at 50 °C for 48 hours, it can be found that calcination at different moderate temperatures has a significant effect on the initial water absorption ratio. The water absorption ratio increases with the increase of the calcination temperature. After calcination at 100 °C, the water absorption ratio of the PC sample in the first 3 hours was significantly increased by 110.6% (compared with 50 °C), while that of the LC³ sample was relatively smaller, which is 64.2%. LC³ sample shows better microstructure and resistance to thermal damage when the temperature is below 100 °C. As the thermal treatment temperature reaches or exceeds 200 °C, as discussed in section 3.1, due to the appearance of damaged cracks, the initial water absorption rate increases significantly, as shown in Figure 5-6 (b) and (d). In this case, the water absorption ratio of LC³ is greater than that of the PC sample.

After 320 hours of water soaking, the samples reached saturation state. The amount of saturated water absorption increases with the increase of the thermal treatment temperature. This may be caused by the dehydroxylation of the hydration products and the destruction of the enclosed pore by the different internal and external pressure (Consolazio et al., 1998). The final water absorption of both PC and LC³ samples after 200 °C thermal treatment is significantly greater than 100°C treatment. For 200, 300 and 400 °C, PC and LC³ samples show similar final water absorption amount.



Figure 5-6. Water absorption of PC (a, b) and $LC^3(c, d)$ after different thermal treatments for 6 hours.

After the sample has reached water saturation, Figure 5-7 shows the change in mass of water evaporation overtime under 50 °C. Compared with Figure 5-6, it can be found that the rate and amount of water evaporation are lower than the water absorption. On the one hand, it may be due to the fact that the adsorption force of water molecules is greater than the kinetic energy of water molecules generated at 50 °C. On the other hand, it may be due to the hydration reaction of unreacted components or the rehydration reaction of dehydroxylated hydration products during the water absorption process, which effectively improves the pore structure (Farage et al., 2003). This may also be the reason why the amount of water evaporated is less than the amount of water through (re)hydration process.
For PC, the thermal treatment temperatures have little effect on the rate and amount of water evaporation. Reversely, in terms of the LC^3 , the water evaporation of the sample after the thermal treatment at 50 °C and 100 °C after 350 hours is about 1g lower than that of the sample at 400 °C. This shows that although the microstructure of the LC^3 samples after heat treatment can be improved by (re)hydration process, there still is part damage that cannot be repaired.



Figure 5-7. Water evaporation of PC (a) and $LC^{3}(b)$ after different thermal treatments.

5.3.4.2 Rehydration and open-pore porosity

To better understand the effects of thermal treatment and water immersion on the open pore structure and hydration products of the samples, the results of water absorption and evaporation is further calculated. Figure 5-8 shows the amount of (re)hydration water of the samples (a), the influence of the dissolution of alkali on the pH value of the solution during the soaking process (b), and the change of the open porosity of the sample after thermal treatment and water saturation (c). By comparing water absorption and evaporation, it can be found that the amount of saturated water absorption is greater than the water evaporation at 50 °C. The difference between the two processes is used to calculate the (re)hydration performance of the sample after thermal treatment (Farage et al., 2003). As shown in Figure 5-8 (a), the (re)hydration of the samples after thermal treatment is the hydration reaction of the unreacted components and the rehydration reaction of the dehydrated components when it encounters water (Farage et al., 2003). After curing for 150 days, the clinker achieved better hydration level. Hence, the (re)hydrated water of the PC sample after the 100 °C heat treatment is small. The (re)hydrated water of the LC³ sample after 100 °C thermal treatment is 3 times that of PC, which may be due to that the replaced 30% calcined clay which did not completely react. The rehydrated water increases with thermally treated temperature. Compared with the PC sample, the LC^3 sample under the same heat treatment temperature showed better rehydration performance. During the soaking process, the precipitated Ca(OH)₂ dissolves in the water, which could have entered the sample under capillary pressure and reacts with the unreacted calcined clay. The dissolved Ca(OH)₂ also diffuses into the deionized water due to the difference in concentration, causing the pH change of the external solution, as shown in Figure 5-8 (b). It can be observed that the leached alkali concentration is related to the thermal treatment temperature. It shows consistent trend with the water absorption performance, which means the leaching alkali mainly comes from the open pore structure. After reaching equilibrium, the pH value of the LC^3 samples solution is lower than that of the PC samples under the same thermal treatment conditions. One reason is that Ca(OH)₂ content in LC³ is lower than that in PC, as analysed by TGA results (as shown in Figure 5-4). On the other hand, it may be attributed to the fact that LC^3 possesses a better microstructure and lower open porosity than PC (Avet and Scrivener, 2018b).

The open porosity of the samples after thermal treatment and the improvement of (re)hydration is shown in Figure 5-8 (c). It can be observed that as the heating temperature increases, the open porosity of the samples gradually increases from 25% to 40%. Farage et al. (Farage et al., 2003) also reported similar results. The open porosity of the LC³ samples shows comparable results with the PC samples under the same thermal treatment conditions. The formation of open pores could be attributed to the following four aspects:

- Part of it is formed during the hardening and curing processes.
- Part of it is formed by the evaporation of free water during the thermal treatment process.
- Part of it is produced due to the dehydration and decomposition of the hydration products (Farage et al., 2003).
- Finally, part of the open pores is attributed to the destruction of the closed pores owing to the thermal treatment (Consolazio et al., 1998).

Except for 100 °C, the open porosity of the samples exposed to different thermal treatment conditions is all found to be significantly modified after resaturation by water absorption. At 100 °C, although there is evaporation of free water and decomposition of AFt and Mc, water saturation has little effect on the total open porosity of the sample. After water saturation, the total open porosity of PC samples treated at 100 °C to 400 °C is 22.9%, 23.6%, 24.0% and 22.1%, respectively. For LC³ samples, the open porosity is 19.1%, 23.0%, 23.4% and 22.3%, respectively. It can be concluded that the LC³ and PC samples treated at temperatures up to 200 °C, 300 °C, and 400 °C reveal a certain degree of reversibility, which may be due to the (re)hydration of the dehydroxylated C-(A)-S-H or the hydration of the initially unhydrated components (Farage et al., 2003). However, the calcination-induced macroscopic cracks on the surface are still present.



Figure 5-8. (Re)hydration property and open porosity change of PC and LC³, (a) (re)hydration water absorption performance, (b) change of pH value of immersion sample solution, (c) open porosity of the samples after thermal treatment and improvement of pore structure after (re)hydration.

5.3.5 SEM analysis

Figure 5-9 shows the microstructure development and crack initiation of LC³ paste at different temperatures. When the thermally treated temperature is lower than 100 °C, although there is free water evaporation and partial bond water dehydration from C-(A)-S-H and AFt, it can be found that there is little obvious thermal damage to the microstructure. The components are tightly connected by hydration products. After 200 °C thermal treatment, several microscopic cracks and pores appear. Fu et al. (Fu et al., 2004) suggested that the occurrence of thermal damage and cracks was mainly attributed to the differences in thermal expansion coefficients between various constituents. The generation of cracks and open pores is also the main reason for the increase in water absorption amount and rate.

At 300 °C, although the dehydration reaction is basically complete, needle-like CSH can still be observed on the surface of the matrix. At this stage, the thermal damage is further aggravated. Interestingly, the AFm phase after dehydration acts as microfiber to bond the matrix together, which may play a role in preventing the cracks to propagate further. As the temperature rises to 400 °C, the hydration products become loosely packed due to dehydration and decomposition of larger fractions of hydration products (Li and Zhang, 2019). After exposing to 400 °C for 6 hours, the width of the crack reaches about 8 μ m with a length of more than 20 μ m. The microstructure degradation leads to a rise in porosity and a dramatic loss in compressive strength (Duan et al., 2016).







5.3.6 FTIR analysis

FTIR spectra can be used to characterize the changes of functional groups environments in cement hydration products (e.g. -OH, Si-O, C-O and Al-O).

Figure 5-10 shows the FTIR spectra of PC and LC3 pastes with different moderate temperature treatments. The peak observed at 3640 cm⁻¹ is consistent with pure portlandite, which is attributed to the symmetric stretching vibration of -OH bond (Hanna et al., 1995). Due to the pozzolanic reaction and higher replacement ratio of PC, the absorption peak at 3640 cm⁻¹ in LC³ is weaker than that in PC. Portlandite has been in a stable state until the temperature reaches 400 °C, after which partial decomposition of portlandite results in a dramatic decrease in the peak at 3640 cm⁻¹, which is observed in Figure 5-4 and Figure 5-11 as well. The broad peak centred at 3400 cm⁻¹ and the peak at 1628 cm⁻¹ is due to symmetric and asymmetric stretching vibrations and bending vibration of -OH in free or chemically bound water (Mollah et al., 2000). At 100 °C, there is still significant free water in the LC³ sample, which may be attributed to the existence of interlayer water in unreacted MK and C-(A)-S-H (Farage et al., 2003).

The broadband centered at around 1412 cm⁻¹ and the peaks at 875 cm⁻¹ and 710 cm⁻¹ are due to the asymmetric stretching vibration and out of plane vibration of CO_3^{2-} in calcium carbonate (Chang and Chen, 2006, Ylmen and Jäglid, 2013). The shoulder peak at 1483 cm⁻¹ may be attributed to different CO_3^{2-} environments, such as Hc and Mc. As the temperature increases, the intensity of the peak located at 1412 cm⁻¹ and 875 cm⁻¹ gradually strengthens. The S-O stretching band presenting those in ettringite or monosulfoaluminate is observed at 1117 cm⁻¹. Compared with 20 °C, the intensity of S-O spectra firstly decreases at 100, 200 and 300 °C, and then increases once the temperature reaching 400 °C.

Si-O-T asymmetric stretching vibration of silicate in PC and LC³ is observed at 953 cm⁻¹ and 960 cm⁻¹, respectively, which indicates that the structure of C-(A)-S-H has changed (Lin et al., 2021). As the calcination temperature increases from ambient temperature to 400 °C, the Si-O band of PC and LC³ shifts slightly toward lower wavenumbers by 36 cm⁻¹ and 20 cm⁻¹, respectively. Sáez Del Bosque et al. (2014) suggested that the Si-O stretching vibration band moving to higher wavenumber during the process of clinker hydration could be considered as the direct proof for C-S-H gel polymerisation (Del Bosque et al., 2014). Therefore, the shift of the Si-O band to lower wavenumbers could be attributed to the depolymerisation or dehydroxylation of C-(A)-S-H during thermal treatment process.



Figure 5-10. FTIR spectra of (a) PC and LC^3 paste, after different moderate temperature treatments, (b) portlandite, (c) limestone and (d) metakaolin.

5.3.7 XRD analysis

The XRD patterns show in Figure 5-11 describe the thermal stability of the products in hydrated PC and LC^3 at different exposure temperatures. Due to the incorporation of calcined clay and limestone, quartz and calcite are present in hardened LC^3 paste. At 50 °C, both PC and LC³ pastes have monocarboaluminate and ettringite phases. It can be observed that the intensity of the peaks belonging to the monocarboaluminate phase in the LC³ paste is stronger than that in PC paste, which is due to the synergistic reaction between calcined clay, limestone and portlandite. However, the hemicarboaluminate phase cannot be detected. Ipavec et al. (2011) found that hemicarboaluminate appeared at early hydration times from 1 to 3 days at 25 °C, and as the hydration progressed, the hemicarboaluminate phase gradually transferred into the monocarboaluminate phase (Ipavec et al., 2011). By the thermal treatment at 100 °C, the ettringite phase decomposes, accompanied by the formation of a small amount of monosulfoaluminate phase. Part of monocarboaluminate is converted into hemicarboaluminate phase by the thermal treatment, which indicates that the thermal stability of hemicarboaluminate is higher than that of monocarboaluminate. At 200, 300, and 400 °C, both hemicarboaluminate and monocarboaluminate phases disappear due to complete dehydroxylation.

It can be observed that the amount of unreacted clinker phases, e.g. dicalcium silicate and tricalcium silicate presented in LC^3 is lower than that in PC system. This is because of the replacement of 50% cement in LC^3 . Another reason is that due to the pozzolanic reactivity of calcined clay and the synergistic reaction of calcined clay and limestone, which consumes the portlandite produced by cement hydration, and reduces the concentration of portlandite in the pore solution, thereby promoting further reaction of clinker (Cao et al., 2021a, Lagier and Kurtis, 2007). The increased diffraction hump between 25° - 35° 20 shows the increased content of amorphous phases at elevated temperatures. This may be attributed to the dehydroxylation of C-(A)-S-H, forming calcium alumina silicate minerals.

The intensity of portlandite in LC^3 is lower than that in PC, which is also observed in TGA and FTIR results. Once the temperature reaches 400 °C, the intensity of the portlandite phase become weaker owing to its partial decomposition.



Figure 5-11. XRD patterns of PC (a) and LC^3 (b) pastes after exposure to different temperatures.

5.3.8 NMR analysis

NMR test has been proven to be an efficient method to examine chemical bonds and polymerization of silica tetrahedron in cement hydration products (Walkley and Provis, 2019). ²⁹Si MAS NMR spectra and spectral deconvolutions for PC and LC³ samples with different moderate temperature treatments are presented in Figure 5-12 (a) and (b), respectively. The presence of the resonance at around -68 ppm, - 71 ppm and part of the resonance at -75 ppm are due to the existing of unhydrated C₃S and C₂S in the cement system (Xue et al., 2021). At 50 °C, the main resonances in both PC and LC³ belong to Q²(1Al), Q⁰ and Q³(1Al). The difference is that there is an

obvious $Q^4(0A1)$ single resonance at around 110 ppm in the LC³ sample, which may be due to the existing of quartz fines in calcined clay (Cao et al., 2021b). The presence of $Q^{4*}(2A1)$, $Q^4(2A1)$ and $Q^4(1A1)$ in the LC³ sample is believed due to the addition of calcined clay, which provides more alumina source to form C-A-S-H, and also the residual of unreacted metakaolin (Cao et al., 2021b).

It can be observed that as the temperature increases, the high-coordination Si units gradually transform into the low-coordination. At 100 °C and 200 °C, the intensity of the resonance centred at around -75 ppm compared with 50 °C significantly increases, which may be caused by the dehydroxylation of ettringite and Mc. For PC, from 300 °C to 400 °C, the intensity of $Q^2(1AI)$, Q^2 and $Q^3(1AI)$ resonances sharply decreases. This indicates that in addition to the dehydroxylation reaction of C-S-H at this temperature, Si-O-Si and Si-O-Al bonds are also destroyed. Compared with the water absorption results, this part of the damage has a certain degree of reversibility and repairability when it encounters water. For LC³, although the $Q^2(1AI)$, $Q^3(1AI)$, $Q^4(4AI)$ and $Q^4(3AI)$ resonances are significantly reduced at 300 °C to 400 °C, there is still a significant $Q^2(1AI)$, $Q^3(1AI)$, $Q^4(4AI)$ and $Q^4(3AI)$ resonances. Avet et al. (2019) suggested that the addition of calcined clay changed the cement hydration products, increasing the C-A-S-H content, and previous research (Collier, 2016) also found C-A-S-H possessing better thermal resistance than C-S-H.

After mathematical deconvolution of MAS NMR spectra (as shown in Figure 5-12 right), the mean chain length (MCL) and Si/Al ratio can be calculated according to the individual resonances (Gao et al., 2017, Wang et al., 2021b). The MCL and Si/Al ratio of PC and LC^3 paste after different moderate temperature treatments are calculated using the following equations and showed in Table 5-3:

$$MCL = \frac{Q1 + \frac{3}{2}Q2(1Al) + Q2}{\frac{1}{2}Q1}$$
Equation 5-5
$$\frac{Si}{Al} = \frac{Q1 + Q2 + Q2(1Al)}{\frac{1}{2}Q2(1Al)}$$
Equation 5-6

After 150 days of hydration, the MCL and Si/Al ratio of C-(A)-S-H in PC sample are 8.72 and 7.69, respectively. Compared with PC, C-(A)-S-H in LC³ sample exhibits longer MCL and lower silicon to aluminum ratio, 12.29 and 6.02, respectively. This

phenomenon is in accordance with previous research. Dai et al. (Dai et al., 2014) found that the MCL and Al/Si ratio will correspondingly increase with increasing metakaolin from 5 wt.% to 30 wt.%. The study of Avet et al. (2019) also revealed that in the LC³ sample, the addition of calcined clay will not change the performance of C-A-S-H, but it will increase the content of C-A-S-H in cement hydration products (Avet et al., 2019). Sevelsted et al. (2013) found that in limestone blended cement, although limestone will accelerate the hydration of alite, it will not affect the length of the C-S-H phase. Hence, metakaolin in calcined clay is the dominant component that affects the chain length of C-A-S-H. As the thermal treatment temperature increases, the MCL of C-A-S-H in the PC and LC³ samples gradually becomes shorter due to the rupture of Si-O-Si and Si-O-Al chemical bonds. The MCL of C-A-S-H in LC³ changes relatively slowly compared with PC. However, at 400 °C, it can be observed that the MCL has been greatly reduced.





Figure 5-12. ²⁹Si MAS NMR data and spectral deconvolutions of PC (a) and LC³ (b) pastes after different moderate temperature treatments.

²⁷Al MAS NMR spectra of PC and LC³ sample treated at different moderate temperatures are shown in Figure 5-13. There are two characteristic spectra in PC and LC³ samples dried at 50 °C, AI^{IV} coordination appearing at 40 - 80 ppm and AI^{VI} coordination appearing at -20 - 20 ppm which exist in AFm phases and TAH phase (Dai et al., 2014). Sevelsted et al. (Sevelsted et al., 2013) indicated that Al^{IV} mainly existed in unreacted clinker as guest-ions or hydration product C-S-H as incorporated ions. In LC³ sample, the appearance of Al^{IV} may also be attributed to the unreacted metakaolin (Cao et al., 2021b). Al^V locating at 20 -40 ppm is mainly bonded in the C-S-H structure to form C-A-S-H structure (Andersen et al., 2006, Walkley and Provis, 2019). It can be found that Al^V in LC³ sample is remarkably

more than that in PC sample, which is consistence with the Si/Al results. After 100 $^{\circ}$ C thermal treatment, the AI^{VI} coordination in PC and LC³ samples is basically unchanged, but the Al^{IV} is shifted to Al^V, indicating that high-temperature curing is contributed to the formation of C-A-S-H.

When the temperature reaches 200 °C, Al^{VI} gradually disappears, accompanied by the appearance of anhydrous spinning sidebands and tetrahedrally coordinated alite and belite. This is the same with ²⁹Si MAS NMR spectra results. Once the temperature reaches 300 °C, the intensity of Al^{VI} resonance sharply reduces due to the dehydroxylation of AFm phases. This is consistent with XRD results, which means AFt and Mc phases will firstly transform to AFm and Hc phases at 100 °C and 200 °C, and in this case, the coordination of aluminum will not be affected.



Figure 5-13. ²⁷Al MAS NMR spectra of the LC³ and PC samples after different moderate temperature treatments. AFm* indicates a group of AFm phases, e.g. monosulfoaluminate, hemicarboaluminate and monocarboaluminate. TAH indicates the hydration product, third aluminate hydrate. A and B represent the presence of aluminum ions centre bands in C_3S and C_2S , respectively.

		PC - Reaction products												
Coordination	Q^{0*}	Q^0	Q^1	$Q^2(1Al)$	Q^2	$Q^3(1Al)$	$Q^4(4Al)$	$Q^4(3Al)$	$Q^4(2Al)$	$Q^4(1Al)$	$Q^4(0Al)$	$Q^4(0Al)$	MCL	Si/Al
Peak site	-68&-	-74	-77	-80	-82	-85	-88	-91	-	-	-	-		
	71													
PC-50	10.4	16.2	10.9	10.6	20.7	14.9	12.8	3.5	-	-	-	-	8.72	7.96
PC-100	11.4	17.7	12.57	11.3	17.0	14.2	12.3	3.5	-	-	-	-	7.40	7.23
PC-200	10.5	17.3	13.8	10.2	14.8	15.9	12.2	5.3	-	-	-	-	6.36	7.61
PC-300	12.5	21.7	15.4	10.9	15.4	11.9	10.1	2.1	-	-	-	-	6.12	7.65
PC-400	16.7	27.0	20.7	12.1	9.6	7.9	3.8	2.2	-	-	-	-	4.68	7.01
LC^3 - Reaction products														
Coordination	Q^{0*}	Q^0	Q^1	$Q^2(1Al)$	Q^2	$Q^3(1Al)$	$Q^4(4Al)$	Q ⁴ (3Al)	$Q^4(2Al)$	Q4*(2Al)	$Q^4(1Al)$	$Q^4(0Al)$	MCL	Si/Al
Peak site	-68&-	-74	-78	-81	-83	-86	-88	-91	-95	-99	-103	-110		
	71													
LC ³ -50	4.6	9.3	5.6	9.8	14.1	11.1	10.0	4.1	3.2	2.6	2.7	22.9	12.29	6.02
LC ³ -100	3.4	7.9	6.1	8.8	14.3	14.6	12.4	4.5	3.5	2.4	2.6	19.5	11.02	6.64
LC ³ -200	3.9	8.5	7.0	9.8	14.0	12.3	7.6	4.3	3.6	3.5	2.9	22.6	10.20	6.29
LC ³ -300	4.7	8.5	8.2	9.3	12.2	12.2	10.0	4.9	3.2	2.2	2.4	22.2	8.38	6.39
LC ³ -400	6.4	10.9	8.9	9.8	10.3	8.5	6.3	3.8	3.9	4.0	3.4	23.6	7.62	5.92

Table 5-3 MCL and Si/Al ratio results from ²⁹Si NMR spectra deconvolution for PC and LC³ pastes after different moderate temperature treatments.

Q^{4*}(2Al): in metakaolin

5.4 Conclusions

In this chapter, the effect of heating at moderate temperatures on the microstructure development and phase evolution of PC and LC^3 products was investigated. Compared with conventional PC, LC^3 exhibited superior performance in terms of pore structure and phase decomposition after moderate temperature exposure. Some important conclusions can be drawn as follows:

- 1. The residual compressive strength of LC^3 and PC mortars kept constant or slightly increased from room temperature to 300 degrees and sharply dropped at 400 °C. The dehydration of AFt, Mc and C-(A)-S-H showed little effect on the strength, and the decomposition of CH will significantly reduce the mechanical properties of the mortar samples.
- 2. PC and LC³ mortars both showed slight shrinkage due to the evaporation of free water. As the temperature exceeds 200 °C, obvious cracks appeared on the surface of PC and LC³ pastes, since the expansion of the crack is greater than the shrinkage caused by the water evaporation, the length of the specimen shows a slight expansion. PC products were more sensitive to temperature than LC³ products in the aspects of length change and crack generation.
- 3. LC³ samples showed better microstructure than PC samples. PC was more sensitive to 100 °C treatment, and the water absorption rate is twice that of LC³ within 3 hours. Compared with PC samples, the LC³ hydration products contain more monocarboaluminate, hemicarboaluminate, C-A-S-H and less calcium hydroxide. In addition, compared with PC samples, LC³ samples subjected to different moderate temperature treatments exhibited comparable or better self-healing ability after water saturation.
- 4. Compared with PC, more Mc and ettringite were observed in the LC³ sample. At 100 °C, it was found that Mc and ettringite gradually transformed into Hc and Ms, respectively, and basically disappeared at 200 °C. The reactive aluminum component in the calcined clay allowed LC³ sample to possess longer MCL and lower Si/Al ratio, resulting in producing more C-A-S-H with better thermal stability. As the thermal treatment temperature increases, the MCL of C-(A)-S-H gradually become shorter, but the Si/Al ratio does not change significantly.

CHAPTER 6. CONCLUSION AND PERSPECTIVES

6.1 Conclusions

This thesis studied the preparation of high-performance fine aggregates and supplementary cementitious materials from waste sandstone by-products, and explored the feasibility and performance of utilizing them as building materials. This research included understanding the physical and chemical properties of sandstone sand and sandstone clay, the influence of sandstone sand on the physical and chemical properties of sandstone sand blended mortar, the exploration of optimal calcination activation parameters and activation mechanism of sandstone clay and the evaluation of pozzolanic reactivity of activated sandstone clay. Finally, the thermal stability of limestone calcined sandstone clay cement after exposure to moderate temperatures was investigated.

In Chapter 3, the workability, mechanical properties, water absorption and ASR properties of mortars prepared from different kinds of sandstone sand were comparatively studied with river sand. It was found that S-sand can be used as high-quality fine aggregate. S-sand possessed smoother microscopic morphology and better particle size distribution. The fine quartz particles below 150 µm accounted for around 15.7 wt. %, which significantly reduced the workability due to the bigger specific surface area. Increasing w/b ratio or application of superplasticizer can remarkably improve workability, the latter was considered to be more suitable for avoiding bleeding problems. With the same w/b and s/b ratios, SS-sand without <150-micron fines exhibited superior compressive and flexural strength properties compared to R sand and FS sand. However, under the similar workability, FS-sand mortar exhibited the best mechanical properties. The application of superplasticizer not only improve the workability of the fresh FS mortar but also densified the microstructure of the hardened mortar.

The study found that although GS-sand showed potential ASR risk, the application of SCMs (i.e. fly ash and activated clay) could effectively reduce the expansion caused by ASR. During the alkali silica reaction process, a strong linear relationship between length change and mass change was calculated, which could be used as an alternative evaluation index for ASR risk evaluation. Due to the damage caused to interfacial transition zone and microstructure, ASR reduced the compressive strength. However, with the progress of ASR, due to the presence of confining stress, the new ASR products filled the cracks caused by expansion, thereby increasing the compressive strength at a specific stage. This mechanism explained the phenomenon that the compressive strength effected by ASR showing a special wave-like pattern.

In the case of sandstone clay, kaolinitic sandstone clay contained around 50% kaolin. Compared to other low-grade kaolinitic by-products, sandstone clays showed the advantage that no further mechanical grinding process was required. When the calcination temperature was 600 °C, the calcination time was at least 3 h, and the dehydroxylation ratio could be improved by prolonging the heating time. Under 700 - 900 °C calcination, isothermal 1 hour was enough. After thermal activation, SEM found that metakaolin generated physical agglomeration, but the agglomeration dissipated when exposed to water. FTIR and NMR results indicated that the pozzolanic reactivity of the calcined clay aroused not only from the kaolinite dehydroxylation reaction, but also from the reactive Al and Si coordination environment generated by the broken of Si-O-Al bond.

The compressive strength of activated sandstone clay mortar at 7 and 28 days showed comparable or even better than that of PC mortar, but the cumulative heat of hydration was lower. It illustrated that when activated sandstone clay was applied as SCM in paste or mortar, in addition to its chemical reactivity, it also exhibited a significant filler effect due to the presence of micro-quartz, which contributed to the development of early compressive strength. Utilizing isothermal calorimetry method to test the pozzolanic reactivity, it was found that the addition of activated sandstone clay enhanced the hydration of C_3A in the early stage. At the same time, the addition of activated sandstone clay reduced the conversion of AFt to AFm, which contributed to the stability of AFt.

Finally, by comparing different techniques and methods, it was found that using TGA-DTG to evaluate the pozzolanic reactivity of activated sandstone clay was very efficient in determining calcium hydroxide consumption by measuring the calcium hydroxide content and the bond water content of the hydration products.

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In Chapter 5, the mechanical properties, phase evolution, microstructure development and (re)hydration properties of LC^3 paste and mortar were investigated to understand their thermal stability under moderate temperatures (100 - 400 °C). Compared with conventional PC, LC^3 exhibited superior performance in terms of pore structure and phase stability after moderate temperature exposure. The residual compressive strength of LC^3 and PC mortars kept constant or slightly increased from room temperature to 300 °C and sharply dropped at 400 °C. The dehydration of AFt, Mc and C-(A)-S-H showed little effect on the strength, and the decomposition of CH significantly reduced the mechanical properties of the mortar samples. PC and LC^3 mortars both showed slight shrinkage due to the evaporation of free water. As the temperature exceeds 200 °C, obvious cracks appeared on the surface of PC and LC^3 paste, since the expansion of the crack is greater than the shrinkage caused by the water evaporation, the length of the specimen showed slight expansion. PC products were more sensitive to temperature than LC^3 products in the aspects of length change and crack generation.

LC³ samples showed better microstructure than PC samples. PC was more sensitive to 100 °C treatment, and the water absorption rate is twice that of LC3 within 3 hours. Compared with PC samples, the LC³ hydration products contain more monocarboaluminate, hemicarboaluminate, C-(A)-S-H and less calcium hydroxide. Compared with PC samples, LC³ samples subjected to different moderate temperature treatments exhibited comparable or better self-healing ability after water saturation. Compared with PC, more Mc and ettringite were observed in the LC³ sample. At 100 °C, it was found that Mc and ettringite gradually transformed into Hc and Ms, respectively, and basically disappeared at 200 °C. The reactive aluminum component in the calcined clay allowed LC³ sample to possess longer MCL and lower Si/Al ratio, resulting in producing more C-A-S-H with better thermal stability. As the thermal treatment temperature increases, the MCL of C-(A)-S-H gradually become shorter, but the Si/Al ratio does not change significantly.

6.2 Perspectives

6.2.1 The issues of fine aggregate

Sandstone sand prepared from sandstone by-products exhibited excellent properties as fine aggregate in mortar. Different from mortar preparation, concrete needs a particular fraction of coarse aggregate, with coarse aggregate and fine aggregate accounting for 65-75 percent of the total volume of concrete. The mechanical characteristics and microstructure of concrete are greatly influenced by the aggregate stacking effect between coarse and fine aggregate. This thesis focuses on the role of sandstone sand in mortar, and the research on the performance of sandstone sand and coarse aggregates with different particle gradations on concrete needs to be further explored.

During the ASR study of sandstone sand, it was found that the length change and mass change caused by ASR have a good linear relationship. Compared with the expansion measurement, the measurement of mass change has simpler and easier operability. The ASR test in this thesis were conducted by the mortar bar method as per the standard of ASTM C1260. However, other methods are also applied to evaluate the ASR property of fine aggregate, such as autoclave curing test. Therefore, it is necessary to compare with more methods to revise and improve the linear relationship.

6.2.2 The issues of low-grade calcined clay

Low-grade calcined clays exhibit promising potential to be used as supplementary cementitious materials as the output of traditional SCMs decreases. Clay contains a variety of minerals, including kaolinite, montmorillonite and illite etc. Different minerals possess different crystalline phases and different silicon and aluminum layers, and the optimal calcination activation parameters for clays containing different kinds of minerals are different. The relevant research in this thesis is based on the kaolinitic clay. Hence, the determination of optimal calcination parameters of low-grade clays coexisting with various minerals has potential research value in the context of broad investigation of low-grade clays for SCM.

The pozzolan assessment method focuses on the CH consumption capacity. However, with the development of cementitious systems (e.g. LC^3 , calcined claybased geopolymer), calcined clay reacts not only with CH in the system, but also with other components such as limestone, sodium hydroxide and sodium silicate, etc. Therefore, for different cementitious systems, it is necessary to explore new evaluation method to assess the chemical reactivity of calcined clays. Additionally, for low-grade clays with a low percent of minerals, the effect of the residual impurities on the performance of cement products is unclear.

It is well known that the added calcined clay can react with calcium hydroxide produced by cement hydration. In concrete, calcium hydroxide from cement hydration crystallizes and accumulates in the positions of pores and ITZ. ITZ is the weak part inside concrete, which seriously affects the mechanical properties and durability of concrete. The effect of the addition of calcined clay on the interface between the mortar matrix and the aggregate is unclear. The capacity to manage the interface of ITZ via secondary hydration of SCMs, such as calcined clay, to improve the mechanical characteristics and durability of concrete is a high-value research topic. The capacity to reconstruction ITZ via "secondary hydration" between calcined clay and calcium hydroxide to improve the mechanical properties and durability has essential research value.

6.2.3 The issues of LC³

Limestone calcined clay cement belongs to a new cement system by combining calcined clay and limestone powder as clinker replacement. The mass fraction of calcined clay and limestone commonly used in LC³ is 2:1, which is determined by the synergistic between MK and limestone. However, clay and limestone quality vary greatly from country to country, which means the reactive components (kaolinite and calcium carbonate) in low-grade clay and limestone are different. Factors such as the fineness of the material will also affect the performance of the material in fresh and hardened cement products. How to propose a series of evaluation indicators according to the material properties (e.g. kaolinite content, fineness, specific surface area) to guide the application of different qualities of calcined clay needs further exploration.

Different from slag, calcined clay belongs to low calcium supplementary cementitious materials. Compared with the traditional single cement replacement, or the combination of slag and calcined clay need further exploration. This will assist to enhance the replacement ratio of cement by SCMs, allowing for further cement reduction without compromising concrete quality.

Finally, the earlier investigations in terms of durability were conducted to assess the single performance of cement products, such as chloride ion penetration, carbonation, acid resistance, sulphate attack, and so on. However, the real service environment of cement products is usually influenced by the coupling of many factors. Therefore, future research should focus on the influence of several coupling variables on the characteristics of calcined clay blended cement and LC^3 .

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APPENDIX

A1 Publications

Journal papers

- Yubin Cao, Yanru Wang, Zuhua Zhang, Yuwei Ma and Hao Wang., (2021). "Recent progress of utilization of activated kaolinitic clay in cementitious construction materials." Composites Part B: Engineering 211: 108636.
- Yubin Cao, Yanru Wang, Zuhua Zhang, Yuwei Ma and Hao Wang. (2021). "Turning sandstone clay into supplementary cementitious material: activation and pozzolanic reactivity evaluation." Composites Part B: Engineering 223: 109137.
- Yubin Cao, Zuhua Zhang, Yanru Wang, Hao Wang. (2021). "Recycled sand from sandstone waste: a new source of high quality fine aggregate." Resources, Conservation & Recycling 179: 106116.
- Yubin Cao, Yanru Wang, Zuhua Zhang, Peng Zhang, Yuwei Ma, Hao Wang. (2022).
 "Thermal stability of limestone calcined clay cement (LC3) at moderate temperatures (100 400 °C)." Cement and Concrete Research, submitted.
- Yanru Wang, Yubin Cao, Zuhua Zhang, Jizhong Huang, Peng Zhang, Yuwei Ma and Hao Wang. (2021) "Study of acidic degradation of alkali-activated materials using synthetic C-(N)-A-S-H and N-A-S-H gels." Composites Part B: Engineering 230, 109510.
- Yanru Wang, Yubin Cao, Yuwei Ma, Shanshan Xiao, Jie Hu and Hao Wang. (2021).
 "Fresh and hardened properties of alkali-activated fly ash/slag binders: effect of fly ash source, surface area, and additives." Journal of Sustainable Cement-Based Materials: 1-24.
- Yanru Wang, Yubin Cao, Zuhua Zhang and Yuwei Ma. (2020). "Effective Utilization of Waste Glass as Cementitious Powder and Construction Sand in Mortar." Materials 13(3): 707.
- Yanru Wang, Yubin Cao, Peng Zhang, Yuwei Ma, Tiejun Zhao, Hao Wang and Zuhua Zhang. (2019). "Water absorption and chloride diffusivity of concrete under the coupling effect of uniaxial compressive load and freeze-thaw cycles." Construction and Building Materials 209: 566-576
- Rui Mo, Penggang Wang, Yanru Wang, Yubin Cao. "Influence of elevated temperatures and cooling regimes on the microstructure development and phases evolution of sodium silicate-activated slag." Materials. Accepted.

Refereed conference papers

- Yubin Cao, Qiuyi Li, Zuhua Zhang, Yanru Wang, "Features of multiple interface structures in recycled aggregate concrete (RAC)," 15th International Congress on the Chemistry of Cement (ICCC 2019), Sep. 16-20, 2019, 514.
- Yanru Wang, Peng Zhang, Zuhua Zhang, Yubin Cao, Hao Wang, "The coupling effect of pressure and freeze-thaw cycles on the durability of concrete," 15th International Congress on the Chemistry of Cement (ICCC 2019), Sep. 16-20, 2019, 510, pp. 370.
- Yanru Wang, Yubin Cao, Zuhua Zhang and Hao Wang, "Understand the intrinsic structure of geopolymer gels of N-A-S-H and C-(N)-A-S-H by synthetic pure precursors," International Union of Laboratories and Experts in Construction Materials, Systems and Structures (RILEM 2019), Aug. 25-30, 2019.



A2. Effects of temperature and alkaline type on the pH value.

A3. Compressive strength development of ternary pastes (metakaolin, limestone and alkaline) with different alkaline conditions.



A4. TG analysis of the ternary pastes under different curing temperatures and ages.





A6. Bond water content of hydration products in the ternary pastes.





A7. FTIR analysis of the ternary pastes under different curing conditions.