

Cementitious Material and Uses Thereof

Technical Field

The present disclosure generally relates to a cementitious composition comprising supplementary
5 cementitious material. The present disclosure further generally relates to a method of producing the cementitious composition.

Background Art

The production process of ordinary Portland Cement (OPC) contributes 8% of total released
anthropogenic CO₂ globally and 50-60% of it is due to the calcination of limestone at 1400-1450 °C. It is
10 unlikely that OPC can be completely replaced in the near future. However, the urgency to develop alternate
low-carbon binders has not gone unnoticed and in this regard, different locally available materials have
investigated as potential supplementary cementitious materials (SCM). The most commonly used SCMs
are either industrial waste such as fly ash, ground granulated blast furnace slag (GGBS), silica fume and
nano silica which contribute to the properties of hardened concrete through their hydraulic and/or
15 pozzolanic activity to the. In addition to these materials natural pozzolans (of volcanic origin), metakaolin
and calcined shale have also been used as SCMs to partially replace OPC. Although the use of metakaolin
as SCM in concrete shows promising mechanical performance, its commercial use on a large scale is
limited owing to its scant availability and high cost. Hence, there is a need to find other sources of SCMs
that can replace OPC.

Summary

In an aspect of the present disclosure, there is provided a cementitious composition comprising:

- (a) Portland cement clinker in an amount of from about 70 wt% to 95 wt% by dry weight based
on the total dry weight of the cementitious composition; and
- (b) supplementary cementitious material in an amount from about 5 wt% to about 30 wt% by dry
25 weight based on the total dry weight of the cementitious composition,
wherein the supplementary cementitious material comprises:
 - (i) calcined clay material produced from heating a clay material at a maximum
temperature of between about 700 °C to about 900 °C;
 - (ii) carbonate material selected from the group consisting of limestone, calcium
30 magnesium carbonate, and mixtures thereof; and
 - (iii) sulphate material selected from the group consisting of gypsum, bassanite, anhydrite,
and mixtures thereof,

wherein the weight ratio of the calcined clay material to the carbonate material is about 1.5:1 to about 2.1:1.

Advantageously, the cementitious composition of the present disclosure solves two problems: firstly to validate the use of raw marine clay as Supplementary Cementitious Material (SCM) in replacing Ordinary Portland Cement; as well as finding a new use for raw marine clay which is normally thought of as industrial waste of no value.

Using calcined clay material derived from raw marine clay as SCM also provides for another advantage, it was discovered that calcination of marine clay takes place at 700 °C to 900 °C, which is a significantly lower temperature as compared to the calcination temperature of clinker (1450 °C). This results in lower energy consumption that directly leads to a smaller carbon footprint. Further the carbonate material used in the cementitious composition of the present disclosure does not need prior calcination, further reducing the carbon footprint of the process.

In another aspect of the present disclosure, there is provided a cementitious composition, comprising:

- (a) Portland cement clinker in an amount of from about 70 wt% to 80 wt% by dry weight based on the total dry weight of the cementitious composition; and
 - (b) supplementary cementitious material in an amount from about 20 wt% to about 30 wt% by dry weight based on the total dry weight of the cementitious composition, wherein the supplementary cementitious material comprises:
 - (i) calcined clay material produced from heating a clay material at a maximum temperature of about 700 °C to about 900 °C, wherein the clay material contains at least about 25 wt% to about 35 wt% kaolinite;
 - (ii) limestone; and
 - (iii) gypsum,
- wherein the weight ratio of the calcined clay material to the limestone is about 2:1 to about 2.1:1.

In a further aspect of the present disclosure, there is provided a method of producing a cementitious composition, comprising:

- (a) heating a clay material at a maximum temperature of about 700 °C to about 900 °C to form a calcined clay material;
- (b) mixing the calcined clay material with a carbonate material selected from the group consisting of limestone, calcium magnesium carbonate, and mixtures thereof, and a sulphate material selected from the group consisting of gypsum, bassanite, anhydrite, and mixtures thereof to form a supplementary cementitious mixture;

(c) blending the supplementary cementitious mixture with Portland cement clinker,

wherein:

the Portland cement clinker is in an amount of from about 70 wt% to 95 wt% by dry weight based on the total dry weight of the cementitious composition;

- 5 the supplementary cementitious material in an amount from about 5 wt% to about 30 wt% by dry weight based on the total dry weight of the cementitious composition;

the weight ratio of the calcined clay material to the carbonate material is about 1.5:1 to about 2.1:1.

Definitions

- 10 Unless otherwise defined herein, scientific and technical terms used in this application shall have the meanings that are commonly understood by those of ordinary skill in the art. Generally, nomenclature used in connection with, and techniques of, chemistry described herein, are those well-known and commonly used in the art.

- 15 Unless the context requires otherwise or specifically stated to the contrary, integers, steps, or elements of the invention recited herein as singular integers, steps or elements clearly encompass both singular and plural forms of the recited integers, steps or elements.

As used herein, the term “clinker” refers to the solid intermediate material produced from the sintering of limestone and aluminosilicate materials during the calcination stage. The same clinker also refers to the intermediate material prior to the formation of the final Portland cement.

- 20 As used herein, the term “supplementary cementitious material” refers to any material that may be used to replace cement clinker in any cement product.

As used herein, the term “marine clay” refers to clay material that are found in coastal regions around the world. They may also be found as a waste by-product from dredging, construction, and reclamation processes.

- 25 As used herein, the term “calcination” refers to the thermal treatment of a material at high temperatures in absence or limited supply of oxygen, to either remove impurities, volatile substances, or to induce thermal decomposition. Accordingly, the term “calcined” refers to the final state of the material that has undergone the process.

- 30 As used herein, the term “cementitious” refers to any material that possess the property akin to cement, i.e. any material that sets, hardens and adheres to other materials.

The word “substantially” does not exclude “completely” e.g. a composition which is “substantially free” from Y may be completely free from Y. Where necessary, the word “substantially” may be omitted from the definition of the invention.

As used herein in the specification and in the claims, the phrase "at least," in reference to a list of one or more elements, should be understood to mean at least one element selected from any one or more of the elements in the list of elements, but not necessarily including at least one of each and every element specifically listed within the list of elements and not excluding any combinations of elements in the list of elements. This definition also allows that elements may optionally be present other than the elements specifically identified within the list of elements to which the phrase "at least one" refers, whether related or unrelated to those elements specifically identified. Thus, as a non-limiting example, "at least one of A and B" (or, equivalently, "at least one of A or B," or, equivalently "at least one of A and/or B") can refer, in one embodiment, to at least one, optionally including more than one, A, with no B present (and optionally including elements other than B); in another embodiment, to at least one, optionally including more than one, B, with no A present (and optionally including elements other than A); in yet another embodiment, to at least one, optionally including more than one, A, and at least one, optionally including more than one, B (and optionally including other elements); etc.

Unless specified otherwise, the terms "comprising" and "comprise", and grammatical variants thereof, are intended to represent "open" or "inclusive" language such that they include recited elements but also permit inclusion of additional, unrecited elements.

As used herein, the term "about", in the context of concentrations of components of the formulations, typically means +/- 5% of the stated value, more typically +/- 4% of the stated value, more typically +/- 3% of the stated value, more typically, +/- 2% of the stated value, even more typically +/- 1% of the stated value, and even more typically +/- 0.5% of the stated value.

Throughout this disclosure, certain embodiments may be disclosed in a range format. It should be understood that the description in range format is merely for convenience and brevity and should not be construed as an inflexible limitation on the scope of the disclosed ranges. Accordingly, the description of a range should be considered to have specifically disclosed all the possible sub-ranges as well as individual numerical values within that range. For example, description of a range such as from 1 to 6 should be considered to have specifically disclosed sub-ranges such as from 1 to 3, from 1 to 4, from 1 to 5, from 2 to 4, from 2 to 6, from 3 to 6 etc., as well as individual numbers within that range, for example, 1, 2, 3, 4, 5, and 6. This applies regardless of the breadth of the range.

Certain embodiments may also be described broadly and generically herein. Each of the narrower species and subgeneric groupings falling within the generic disclosure also form part of the

disclosure. This includes the generic description of the embodiments with a proviso or negative limitation removing any subject matter from the genus, regardless of whether or not the excised material is specifically recited herein.

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Brief Description of Drawings

The accompanying drawings illustrate disclosed embodiments and serve to explain the principles of the disclosed embodiments. It is to be understood, however, that the drawings are designed for purposes of illustration only, and not as a definition of the limits of the invention.

Fig. 1

- 10 Figure 1 is a graph showing the particle size distribution of Ordinary Portland cement (Portland cement clinker) and marine clay.

Fig. 2

Figure 2 is a graph showing the mass loss and Differential Thermal Analysis (DTA) curves obtained from Thermogravimetric Analysis (TGA) tests.

- 15 **Fig. 3**

Figure 3 is a series of photos showing the preparation of calcined marine clay from raw marine clay.

Fig. 4

Figure 4 are graphs showing the X-ray Diffraction (XRD) spectrums of marine clay (MC) at room temperature, and after calcination at different temperatures.

- 20 **Fig. 5**

Figure 5 is a graph showing the Magic Spinning Angle Nuclear Magnetic Resonance (MAS NMR) spectrum of ^{27}Al nuclei in marine clay at room temperature, and after calcination at different temperatures.

Fig. 6

- 25 Figure 6 is a graph showing the Magic Spinning Angle Nuclear Magnetic Resonance (MAS NMR) spectrum of ^{29}Si nuclei in marine clay at room temperature, and after calcination at different temperatures.

Fig. 7

Figure 7 is a graph showing the heat evolution rate of cementitious compositions comprising clay material calcined at different temperatures.

Fig. 8

- 5 Figure 8 is a graph showing the cumulative heat evolution of cementitious compositions comprising clay material calcined at different temperatures.

Fig. 9

Figure 9 is a diagram showing the preparation of cementitious compositions comprising either partial or total replacement of the Portland cement clinker with calcined clay material.

10 **Fig. 10**

Figure 10 is a graph showing the heat evolution rate of cementitious compositions comprising different amounts of sulphate material.

Fig. 11

- 15 Figure 11 is a graph showing the cumulative heat evolution of cementitious compositions comprising different amounts of sulphate material.

Fig. 12

Figure 12 is a graph showing the compressive strength results of different cementitious compositions.

Fig. 13a

- 20 Figure 13a is a graph showing the thermal conductivity of different cementitious compositions under different curing conditions.

Fig. 13b

Figure 13b is a graph showing the thermal diffusivity of different cementitious compositions under different curing conditions.

Fig. 13c

- 25 Figure 13c is a graph showing the volumetric heat capacities of different cementitious compositions under different curing conditions.

Fig. 14

Figure 14 is a graph showing the compressive strength of mortar samples made according to the procedure in Example 8 under different curing conditions.

Fig. 15

- 5 Figure 15 is a graph showing the X-Ray Diffraction (XRD) spectrums of marine clay calcined at 800 °C, for different durations.

Fig. 16a

Figure 16a is a graph showing the cumulative heat evolution of cementitious compositions prepared from clay material calcined under different calcination durations.

10 **Fig. 16b**

Figure 16b is a graph showing the hydration heat flow for the first 1 hour, of cementitious compositions prepared from clay material calcined under different calcination durations.

Fig. 16c

- 15 Figure 16c is a graph showing the hydration heat flow for the first 48 hours, of cementitious compositions prepared from clay material calcined under different calcination durations.

Fig. 17

Figure 17 is a graph showing the compressive strength of cementitious compositions prepared from clay material calcined at different maximum temperatures.

20 **Detailed Disclosure of Drawings**

- Referring to Fig. 3, calcined clay material of the present invention is generally prepared as follows: clay material (raw marine clay) (1) is first manually broken down by manual crushing to provide crushed clay material (2), after which it is grinded in a ball miller for 5 minutes (3) and sieved through a 150 µm sieve to provide fine clay material (4). The fine clay material is then calcined inside
25 a furnace at 900 °C (5) to provide calcined clay material (6). The calcined clay material is then further milled in a ball miller for 1 minute (7) to provide the final calcined clay material used in the present invention.

Referring to Fig. 9, the cementitious composition of the present invention is generally prepared as follows: clay material (raw marine clay) (1) is first manually broken down by manual

crushing (8) to provide crushed clay material (2), after which it is grinded in a ball miller for 5 minutes (3) and sieved through a 150 μm sieve to provide fine clay material (4). The fine clay material is then calcined inside a furnace at 900 °C (5) to provide calcined clay material (6). The calcined clay material is then further milled in a ball miller for 1 minute (7) to provide the final calcined clay material (9).

- 5 To form a Limestone Calcined Clay Cement (LC³) composition (LC³ mix, 12) the final calcined marine clay (9) is mixed with Portland cement clinker, limestone, gypsum, sand, water, and superplasticizer as needed (11) to provide the LC³ composition (12) in Example 7. To form a mortar composition (MC mix, 13), the final calcined marine clay (9) was mixed with Portland cement clinker, sand, water, and superplasticizer if needed (10) to provide the MC composition (13) in Example 6.

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Detailed Disclosure of Embodiments

The present disclosure provides for a cementitious composition comprising:

- (a) Portland cement clinker in an amount of from about 70 wt% to 95 wt% by dry weight based on the total dry weight of the cementitious composition; and
- 15 (b) supplementary cementitious material in an amount from about 5 wt% to about 30 wt% by dry weight based on the total dry weight of the cementitious composition, wherein the supplementary cementitious material comprises:
- (i) calcined clay material produced from heating a clay material at a maximum temperature of between about 700 °C to about 900 °C;
- 20 (ii) carbonate material selected from the group consisting of limestone, calcium magnesium carbonate, and mixtures thereof; and
- (iii) sulphate material selected from the group consisting of gypsum, bassanite, anhydrite, and mixtures thereof,
- wherein the weight ratio of the calcined clay material to the carbonate material is about 1.5:1 to about 2.1:1.
- 25

The present invention relates to the use of calcined marine clay in the replacement of cement as a supplementary cementitious material. The present invention advantageously reduces the amount of clinker and/or cement utilization in the construction industry, by using marine clay as a major component of supplementary cementitious material. It is known that marine clay is a major waste material with no known purpose. Hence, the present invention also aims to convert a previously useless waste material into a new material with potential new uses.

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The current problem with obtaining calcined marine clay suitable as a supplementary cementitious material is that the conditions that would activate marine clay are unknown. Owing to the different

compositions of marine clay in different regions of the world, operating and treatment conditions are unlikely to be applicable for all marine clay sources. Hence, various components that make up the supplementary cementitious material require rigorous optimization; for example, calcined clay material, gypsum, limestone, calcination temperature of the clay material and its holding duration, and all factors
5 need to be taken into consideration in order to maintain the structural strength that the new cement provides.

The cementitious composition may also be referred to as a Limestone Calcined Clay Cement (LC³) binder. The LC³ binder may be a ternary binder of calcined marine clay, limestone, gypsum and OPC. In other words, the LC³ binder may comprise or consist of OPC and supplementary cementitious material. The term LC³ may be also be used to refer to the supplementary cementitious material.

10 Compositions comprising cementitious composition, sand, water and optionally superplasticizer may be referred to as LC³ mixes. In other words, LC³ mixes may comprise OPC, calcined marine clay, limestone, gypsum, sand, water and optionally superplasticizer, or LC³ mixes may comprise LC³ binder, sand, water and optionally superplasticizer.

The term "MC mixes" as used herein refers to compositions containing OPC, calcined marine clay,
15 sand, water and optionally superplasticizer (i.e. without limestone and gypsum).

Various percentages of the Portland cement clinker may be used in the cementitious composition of the present invention. For example, the Portland cement clinker may be present, by dry weight of the total dry weight of the cementitious composition, in at least about 50 wt%, at least about 55 wt%, at least about 60 wt%, at least about 65 wt%, at least about 70 wt%, at least about 75 wt%, at least about 80 wt%,
20 at least about 85 wt%, at least about 90 wt%, at least about 95 wt%, from about 50 wt% to about 95 wt%, from about 55 wt% to about 95 wt%, from about 60 wt% to about 95 wt%, from about 65 wt% to about 95 wt%, from about 70 wt% to about 95 wt%, from about 75 wt% to about 95 wt%, from about 80 wt% to about 95 wt%, from about 85 wt% to about 95 wt%, from about 90 wt% to about 95 wt%, from about 50 wt% to about 90 wt%, from about 55 wt% to about 90 wt%, from about 60 wt% to about 90 wt%, from
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from about 55 wt% to about 60 wt%, from about 50 wt% to about 55 wt%, about 50 wt%, about 55 wt%, about 60 wt%, about 65 wt%, about 70 wt%, about 75 wt%, about 80 wt%, about 85 wt%, about 90 wt%, about 95 wt%, or any range or value therebetween. In a preferred embodiment, the Portland cement clinker is present in about 50 wt% to about 95 wt% by dry weight of the total dry weight of the cementitious composition of the present invention. In yet another preferred embodiment the Portland cement clinker is present in about 70 wt% to about 95 wt% by dry weight of the total dry weight of the cementitious composition of the present invention. In a further preferred embodiment, the Portland cement clinker is present in about 70 wt% to about 80 wt% by dry weight of the total dry weight of the cementitious composition of the present invention. In yet another preferred embodiment, the Portland cement clinker is present in about 70 wt% by dry weight of the total dry weight of the cementitious composition of the present invention.

The supplementary cementitious material referred to in the present invention may comprise calcined clay material, limestone, gypsum, or any mixtures and combinations thereof. Supplementary cementitious material may also be referred to herein as LC³. Supplementary cementitious materials advantageously require a lower calcination temperature to activate in comparison to Portland cement clinker, or Ordinary Portland Cement (OPC). At a lower calcination temperature, less energy is thus needed to convert the raw material into the working form, leading to a smaller carbon footprint, as well as less energy costs. Thus, it is highly desirable to find a complete replacement for OPC, or to replace as much of the OPC as possible without negatively impacting its industrial strength.

To this end, the inventors have surprisingly discovered that raw marine clay, commonly part of the industrial waste products from dredging and reclamation works comprise workable amounts of kaolinite. Kaolinite, when exposed to high temperature of at least 500 °C for long durations of time, is converted into metakaolin. Metakaolin is an extremely useful pozzolan that possesses high cementitious properties. Metakaolin is also generally more easily sourced compared to calcined shale and other pozzolans like fly ash and blast furnace slag. Fly ash and blast furnace slag are found as waste from other industries and incineration processes; thus, they are extremely limited in availability. Calcined shale may be used, but its high concentration of calcium carbonate or calcium oxide also means lower silicon dioxide (SiO₂) and alumina (Al₂O₃) concentrations. As silicon dioxide and alumina is desired for forming strong bonds during the hydration phase, metakaolin is a much more useful alternative to calcined clay.

However, kaolinite and metakaolin sources in general are rare and expensive, hence, they are not usually used as substitutes for cement. Marine clay, as discovered, possesses workable amounts of kaolinite that may be converted to metakaolin upon calcination. Further, the composition of marine clay does not hamper its potential as a replacement for cement. In this present disclosure, the inventors have shown that calcined marine clay is viable as a supplementary cementitious material. Hence, in replacing Portland cement clinker with calcined marine clay, the inventors have discovered a cementitious composition that

not only has comparative compressive strength to ordinary Portland cement compositions, but also has a smaller carbon footprint and requires smaller amounts of energy to form.

To this end, any material that comprises kaolinite may be used for the present invention. Clay material dredged from Singapore waters are surprisingly useful to that effect. It is desirable that the clay material contains kaolinite by weight based on the total weight of the clay material, at least about 15 wt%, at least about 20 wt%, at least about 25 wt%, at least about 29 wt%, at least about 30 wt%, at least about 35 wt%, at least about 40 wt%, at least about 45 wt%, at least about 50 wt%, at least about 61 wt%, at least about 70 wt%, at least about 80 wt%, at least about 90 wt%, about 15 wt% to about 90 wt%, about 20 wt% to about 90 wt%, about 25 wt% to about 90 wt%, about 29 wt% to about 90 wt%, about 30 wt% to about 90 wt%, about 35 wt% to about 90 wt%, about 40 wt% to about 90 wt%, about 45 wt% to about 90 wt%, about 50 wt% to about 90 wt%, about 61 wt% to about 90 wt%, about 70 wt% to about 90 wt%, about 80 wt% to about 90 wt%, about 15 wt% to about 80 wt%, about 20 wt% to about 80 wt%, about 25 wt% to about 80 wt%, about 29 wt% to about 80 wt%, about 30 wt% to about 80 wt%, about 35 wt% to about 80 wt%, about 40 wt% to about 80 wt%, about 45 wt% to about 80 wt%, about 50 wt% to about 80 wt%, about 61 wt% to about 80 wt%, about 70 wt% to about 80 wt%, about 15 wt% to about 70 wt%, about 20 wt% to about 70 wt%, about 25 wt% to about 70 wt%, about 29 wt% to about 70 wt%, about 30 wt% to about 70 wt%, about 35 wt% to about 70 wt%, about 40 wt% to about 70 wt%, about 45 wt% to about 70 wt%, about 50 wt% to about 70 wt%, about 61 wt% to about 70 wt%, about 15 wt% to about 61 wt%, about 20 wt% to about 61 wt%, about 25 wt% to about 61 wt%, about 29 wt% to about 61 wt%, about 30 wt% to about 61 wt%, about 35 wt% to about 61 wt%, about 40 wt% to about 61 wt%, about 45 wt% to about 61 wt%, about 50 wt% to about 61 wt%, about 15 wt% to about 50 wt%, about 20 wt% to about 50 wt%, about 25 wt% to about 50 wt%, about 29 wt% to about 50 wt%, about 30 wt% to about 50 wt%, about 35 wt% to about 50 wt%, about 40 wt% to about 50 wt%, about 45 wt% to about 50 wt%, about 15 wt% to about 45 wt%, about 20 wt% to about 45 wt%, about 25 wt% to about 45 wt%, about 29 wt% to about 45 wt%, about 30 wt% to about 45 wt%, about 35 wt% to about 45 wt%, about 40 wt% to about 45 wt%, about 15 wt% to about 40 wt%, about 20 wt% to about 40 wt%, about 25 wt% to about 40 wt%, about 29 wt% to about 40 wt%, about 30 wt% to about 40 wt%, about 35 wt% to about 40 wt%, about 15 wt% to about 35 wt%, about 20 wt% to about 35 wt%, about 25 wt% to about 35 wt%, about 29 wt% to about 35 wt%, about 30 wt% to about 35 wt%, about 15 wt% to about 30 wt%, about 20 wt% to about 30 wt%, about 25 wt% to about 30 wt%, about 29 wt% to about 30 wt%, about 15 wt% to about 29 wt%, about 20 wt% to about 29 wt%, about 25 wt% to about 29 wt%, about 15 wt% to about 25 wt%, about 20 wt% to about 25 wt%, about 15 wt%, about 20 wt%, about 25 wt%, about 29 wt%, about 30 wt%, about 35 wt%, about 40 wt%, about 45 wt%, about 50 wt%, about 61 wt%, about 70 wt%, about 80 wt%, about 90 wt%, or any ranges or values therebetween. In some preferred embodiments, the clay material comprises at least about 25 wt% kaolinite. In some other preferred embodiments, the clay material comprises about 61 wt% kaolinite. In some further preferred embodiments, the clay material comprises about 25 wt% to

about 35 wt% kaolinite. In yet another further preferred embodiment, the clay material comprises about 29 wt% kaolinite.

Kaolinite can be converted into the active metakaolin at elevated temperatures. However, the appropriate temperature for fully converting all kaolinite into the metakaolin has not been investigated in full detail. Hence, the present inventors have discovered appropriate temperatures by which raw marine clay, or kaolinite-containing clay material in general, may be calcined and converted into metakaolin-containing calcined clay material.

In some embodiments, calcined clay material may be produced by heating clay material or raw marine clay at various temperatures to convert the kaolinite to the active metakaolin. For example, the calcined clay material may be produced from heating the clay material at a maximum temperature of at least about 500 °C, at least about 550 °C, at least about 600 °C, at least about 650 °C, at least about 700 °C, at least about 750 °C, at least about 800 °C, at least about 850 °C, at least about 900 °C, at least about 950 °C, at least about 1000 °C, at least about 1050 °C, at least about 1100 °C, at least about 1200 °C, about 500 °C to about 1200 °C, about 550 °C to about 1200 °C, about 600 °C to about 1200 °C, about 650 °C to about 1200 °C, about 700 °C to about 1200 °C, about 750 °C to about 1200 °C, about 800 °C to about 1200 °C, about 850 °C to about 1200 °C, about 900 °C to about 1200 °C, about 950 °C to about 1200 °C, about 1000 °C to about 1200 °C, about 1050 °C to about 1200 °C, about 1100 °C to about 1200 °C, about 500 °C to about 1100 °C, about 550 °C to about 1100 °C, about 600 °C to about 1100 °C, about 650 °C to about 1100 °C, about 700 °C to about 1100 °C, about 750 °C to about 1100 °C, about 800 °C to about 1100 °C, about 850 °C to about 1100 °C, about 900 °C to about 1100 °C, about 950 °C to about 1100 °C, about 1000 °C to about 1100 °C, about 1050 °C to about 1100 °C, about 500 °C to about 1050 °C, about 550 °C to about 1050 °C, about 600 °C to about 1050 °C, about 650 °C to about 1050 °C, about 700 °C to about 1050 °C, about 750 °C to about 1050 °C, about 800 °C to about 1050 °C, about 850 °C to about 1050 °C, about 900 °C to about 1050 °C, about 950 °C to about 1050 °C, about 1000 °C to about 1050 °C, about 500 °C to about 1000 °C, about 550 °C to about 1000 °C, about 600 °C to about 1000 °C, about 650 °C to about 1000 °C, about 700 °C to about 1000 °C, about 750 °C to about 1000 °C, about 800 °C to about 1000 °C, about 850 °C to about 1000 °C, about 900 °C to about 1000 °C, about 950 °C to about 1000 °C, about 500 °C to about 950 °C, about 550 °C to about 950 °C, about 600 °C to about 950 °C, about 650 °C to about 950 °C, about 700 °C to about 950 °C, about 750 °C to about 950 °C, about 800 °C to about 950 °C, about 850 °C to about 950 °C, about 900 °C to about 950 °C, about 500 °C to about 900 °C, about 550 °C to about 900 °C, about 600 °C to about 900 °C, about 650 °C to about 900 °C, about 700 °C to about 900 °C, about 750 °C to about 900 °C, about 800 °C to about 900 °C, about 850 °C to about 900 °C, about 500 °C to about 850 °C, about 550 °C to about 850 °C, about 600 °C to about 850 °C, about 650 °C to about 850 °C, about 700 °C to about 850 °C, about 750 °C to about 850 °C, about 800 °C to about 850 °C, about 500 °C to about 800 °C, about 550 °C to about 800 °C, about 600 °C to about 800 °C, about 650 °C to about 800 °C, about 700 °C to about 800 °C, about 750 °C to about 800 °C, about 500 °C to about 750 °C, about 550

°C to about 750 °C, about 600 °C to about 750 °C, about 650 °C to about 750 °C, about 700 °C to about 750 °C, about 500 °C to about 700 °C, about 550 °C to about 700 °C, about 600 °C to about 700 °C, about 650 °C to about 700 °C, about 500 °C to about 650 °C, about 550 °C to about 650 °C, about 600 °C to about 650 °C, about 500 °C to about 600 °C, about 550 °C to about 600 °C, about 500 °C to about 550 °C, about 500 °C, about 550 °C, about 600 °C, about 650 °C, about 700 °C, about 750 °C, about 800 °C, about 850 °C, about 900 °C, about 950 °C, about 1000 °C, about 1050 °C, about 1100 °C, about 1200 °C, or any range of value therebetween. In some preferred embodiments, the calcined clay material is produced from heating the clay material at a maximum temperature of between about 700 °C to about 900 °C. In a further preferred embodiment, the calcined clay material is produced from heating the clay material at a maximum temperature of about 900 °C.

In some embodiments, the calcined clay material is produced by first heating the clay material at a steady rate up to a maximum temperature, whereafter the maximum temperature is held for a certain period to complete the calcination. As the cement industry currently performs calcination by a steady-rate ramping of temperature, the cementitious composition of the present invention can thus be easily scaled up and produced using existing technology.

In some embodiments, the calcined clay material may be produced from heating the clay material up to a maximum temperature as disclosed herein, at a rate of at least about 2 °C per minute, at least about 4 °C per minute, at least about 5 °C per minute, at least about 6 °C per minute, at least about 8 °C per minute, at least about 10 °C per minute, at least about 12 °C per minute, at least about 14 °C per minute, at least about 15 °C per minute, at least about 16 °C per minute, at least about 18 °C per minute, at least about 20 °C per minute, about 2 °C per minute to about 20 °C per minute, about 4 °C per minute to about 20 °C per minute, about 5 °C per minute to about 20 °C per minute, about 6 °C per minute to about 20 °C per minute, about 8 °C per minute to about 20 °C per minute, about 10 °C per minute to about 20 °C per minute, about 12 °C per minute to about 20 °C per minute, about 14 °C per minute to about 20 °C per minute, about 15 °C per minute to about 20 °C per minute, about 16 °C per minute to about 20 °C per minute, about 18 °C per minute to about 20 °C per minute, about 2 °C per minute to about 18 °C per minute, about 4 °C per minute to about 18 °C per minute, about 5 °C per minute to about 18 °C per minute, about 6 °C per minute to about 18 °C per minute, about 8 °C per minute to about 18 °C per minute, about 10 °C per minute to about 18 °C per minute, about 12 °C per minute to about 18 °C per minute, about 14 °C per minute to about 18 °C per minute, about 15 °C per minute to about 18 °C per minute, about 16 °C per minute to about 18 °C per minute, about 2 °C per minute to about 16 °C per minute, about 4 °C per minute to about 16 °C per minute, about 5 °C per minute to about 16 °C per minute, about 6 °C per minute to about 16 °C per minute, about 8 °C per minute to about 16 °C per minute, about 10 °C per minute to about 16 °C per minute, about 12 °C per minute to about 16 °C per minute, about 14 °C per minute to about 16 °C per minute, about 15 °C per minute to about 16 °C per minute, about 2 °C per minute to about 15 °C per minute, about 4 °C per minute to about 15 °C per minute, about 5 °C per minute to about 15 °C per minute, about 6 °C per minute

to about 15 °C per minute, about 8 °C per minute to about 15 °C per minute, about 10 °C per minute to about 15 °C per minute, about 12 °C per minute to about 15 °C per minute, about 14 °C per minute to about 15 °C per minute, about 2 °C per minute to about 14 °C per minute, about 4 °C per minute to about 14 °C per minute, about 5 °C per minute to about 14 °C per minute, about 6 °C per minute to about 14 °C per minute, about 8 °C per minute to about 14 °C per minute, about 10 °C per minute to about 14 °C per minute, about 12 °C per minute to about 14 °C per minute, about 2 °C per minute to about 12 °C per minute, about 4 °C per minute to about 12 °C per minute, about 5 °C per minute to about 12 °C per minute, about 6 °C per minute to about 12 °C per minute, about 8 °C per minute to about 12 °C per minute, about 10 °C per minute to about 12 °C per minute, about 2 °C per minute to about 10 °C per minute, about 4 °C per minute to about 10 °C per minute, about 5 °C per minute to about 10 °C per minute, about 6 °C per minute to about 10 °C per minute, about 8 °C per minute to about 10 °C per minute, about 2 °C per minute to about 8 °C per minute, about 4 °C per minute to about 8 °C per minute, about 5 °C per minute to about 8 °C per minute, about 6 °C per minute to about 8 °C per minute, about 2 °C per minute to about 6 °C per minute, about 4 °C per minute to about 6 °C per minute, about 5 °C per minute to about 6 °C per minute, about 2 °C per minute to about 5 °C per minute, about 4 °C per minute to about 5 °C per minute, about 2 °C per minute to about 4 °C per minute, about 2 °C per minute, about 4 °C per minute, about 5 °C per minute, about 6 °C per minute, about 8 °C per minute, about 10 °C per minute, about 12 °C per minute, about 14 °C per minute, about 15 °C per minute, about 16 °C per minute, about 18 °C per minute, about 20 °C per minute, or any ranges or values therebetween. In a preferred embodiment, the calcined clay material may be produced from heating the clay material at a rate of about 5 °C per minute to about 15 °C per minute up to a maximum temperature as disclosed herein. In a further preferred embodiment, the calcined clay material may be produced from heating the clay material at a rate of about 10 °C per minute up to a maximum temperature as disclosed herein.

After the maximum temperature is reached, the clay material may need to be maintained at the maximum temperature for a minimum duration in order to fully convert all the kaolinite in the clay material into the active metakaolin form. In some embodiments, the maximum temperature is maintained for at least about 1 hour, at least about 1.25 hours, at least about 1.5 hours, at least about 1.75 hours, at least about 2 hours, at least about 2.25 hours, at least about 2.5 hours, at least about 2.75 hours, at least about 3 hours, at least about 3.25 hours, at least about 3.5 hours, at least about 4 hours, about 1 hour to about 4 hours, about 1.25 hours to about 4 hours, about 1.5 hours to about 4 hours, about 1.75 hours to about 4 hours, about 2 hours to about 4 hours, about 2.25 hours to about 4 hours, about 2.5 hours to about 4 hours, about 2.75 hours to about 4 hours, about 3 hours to about 4 hours, about 3.25 hours to about 4 hours, about 3.5 hours to about 4 hours, about 1 hour to about 3.5 hours, about 1.25 hours to about 3.5 hours, about 1.5 hours to about 3.5 hours, about 1.75 hours to about 3.5 hours, about 2 hours to about 3.5 hours, about 2.25 hours to about 3.5 hours, about 2.5 hours to about 3.5 hours, about 2.75 hours to about 3.5 hours, about 3 hours to about 3.5 hours, about 3.25 hours to about 3.5 hours, about 1 hour to about 3.25 hours, about 1.25

hours to about 3.25 hours, about 1.5 hours to about 3.25 hours, about 1.75 hours to about 3.25 hours, about 2 hours to about 3.25 hours, about 2.25 hours to about 3.25 hours, about 2.5 hours to about 3.25 hours, about 2.75 hours to about 3.25 hours, about 3 hours to about 3.25 hours, about 1 hour to about 3 hours, about 1.25 hours to about 3 hours, about 1.5 hours to about 3 hours, about 1.75 hours to about 3 hours, about 2 hours to about 3 hours, about 2.25 hours to about 3 hours, about 2.5 hours to about 3 hours, about 2.75 hours to about 3 hours, about 1 hour to about 2.75 hours, about 1.25 hours to about 2.75 hours, about 1.5 hours to about 2.75 hours, about 1.75 hours to about 2.75 hours, about 2 hours to about 2.75 hours, about 2.25 hours to about 2.75 hours, about 2.5 hours to about 2.75 hours, about 1 hour to about 2.5 hours, about 1.25 hours to about 2.5 hours, about 1.5 hours to about 2.5 hours, about 1.75 hours to about 2.5 hours, about 2 hours to about 2.5 hours, about 2.25 hours to about 2.5 hours, about 1 hour to about 2.25 hours, about 1.25 hours to about 2.25 hours, about 1.5 hours to about 2.25 hours, about 1.75 hours to about 2.25 hours, about 2 hours to about 2.25 hours, about 1 hour to about 2 hours, about 1.25 hours to about 2 hours, about 1.5 hours to about 2 hours, about 1.75 hours to about 2 hours, about 1 hour to about 1.75 hours, about 1.25 hours to about 1.75 hours, about 1.5 hours to about 1.75 hours, about 1 hour to about 1.5 hours, about 1.25 hours to about 1.5 hours, about 1 hour to about 1.25 hours, about 1 hour, about 1.25 hours, about 1.5 hours, about 1.75 hours, about 2 hours, about 2.25 hours, about 2.5 hours, about 2.75 hours, about 3 hours, about 3.25 hours, about 3.5 hours, about 4 hours, or any ranges or values therebetween. In a preferred embodiment, the maximum temperature is maintained for at least 1 hour. In yet a preferred embodiment, the maximum temperature is maintained for at least 2 hours.

20 In some embodiments, the calcined clay material is produced from heating the clay material at a rate of about 5 °C to about 15 °C per minute up to a maximum temperature of about 500 °C to about 900 °C, and the maximum temperature is maintained for at least 1 hour. In some embodiments, the calcined clay material is produced from heating the clay material at a rate of about 10 °C per minute up to a maximum temperature of about 500 °C to about 900 °C, and the maximum temperature is maintained for at least 1 hour. In some embodiments, the calcined clay material is produced from heating the clay material at a rate of about 5 °C to about 15 °C per minute up to a maximum temperature of about 700 °C to about 900 °C, and the maximum temperature is maintained for at least 1 hour. In some embodiments, the calcined clay material is produced from heating the clay material at a rate of about 10 °C per minute up to a maximum temperature of about 700 °C to about 900 °C, and the maximum temperature is maintained for at least 1 hour. In some embodiments, the calcined clay material is produced from heating the clay material at a rate of about 5 °C to about 15 °C per minute up to a maximum temperature of about 900 °C, and the maximum temperature is maintained for at least 1 hour. In some embodiments, the calcined clay material is produced from heating the clay material at a rate of about 10 °C per minute up to a maximum temperature of about 900 °C, and the maximum temperature is maintained for at least 1 hour. In some embodiments, the calcined clay material is produced from heating the clay material at a rate of about 5 °C to about 15 °C per minute up to a maximum temperature of about 500 °C to about 900 °C, and the maximum temperature is maintained for at least 2 hours. In some embodiments, the calcined clay material is produced from

heating the clay material at a rate of about 10 °C per minute up to a maximum temperature of about 500 °C to about 900 °C, and the maximum temperature is maintained for at least 2 hours. In some embodiments, the calcined clay material is produced from heating the clay material at a rate of about 5 °C to about 15 °C per minute up to a maximum temperature of about 700 °C to about 900 °C, and the maximum temperature is maintained for at least 2 hours. In some embodiments, the calcined clay material is produced from heating the clay material at a rate of about 10 °C per minute up to a maximum temperature of about 700 °C to about 900 °C, and the maximum temperature is maintained for at least 2 hours. In some embodiments, the calcined clay material is produced from heating the clay material at a rate of about 5 °C to about 15 °C per minute up to a maximum temperature of about 900 °C, and the maximum temperature is maintained for at least 2 hours. In some embodiments, the calcined clay material is produced from heating the clay material at a rate of about 10 °C per minute up to a maximum temperature of about 900 °C, and the maximum temperature is maintained for at least 2 hours.

Various percentages of the supplementary cementitious material may be present in the cementitious composition by dry weight based on the total dry weight of the cementitious composition. Generally, the amount of cement that may be replaced is proportionate to the amount of metakaolin (formed from the calcination of clay material) in the supplementary cementitious material. In some embodiments, the supplementary cementitious material may be present, by dry weight of the total dry weight of the cementitious composition, in an amount of at least about 5 wt%, at least about 10 wt%, at least about 15 wt%, at least about 20 wt%, at least about 25 wt%, at least about 30 wt%, at least about 35 wt%, at least about 40 wt%, at least about 45 wt%, at least about 50 wt%, from about 5 wt% to about 50 wt%, from about 10 wt% to about 50 wt%, from about 15 wt% to about 50 wt%, from about 20 wt% to about 50 wt%, from about 25 wt% to about 50 wt%, from about 30 wt% to about 50 wt%, from about 35 wt% to about 50 wt%, from about 40 wt% to about 50 wt%, from about 45 wt% to about 50 wt%, from about 5 wt% to about 45 wt%, from about 10 wt% to about 45 wt%, from about 15 wt% to about 45 wt%, from about 20 wt% to about 45 wt%, from about 25 wt% to about 45 wt%, from about 30 wt% to about 45 wt%, from about 35 wt% to about 45 wt%, from about 40 wt% to about 45 wt%, from about 5 wt% to about 40 wt%, from about 10 wt% to about 40 wt%, from about 15 wt% to about 40 wt%, from about 20 wt% to about 40 wt%, from about 25 wt% to about 40 wt%, from about 30 wt% to about 40 wt%, from about 35 wt% to about 40 wt%, from about 5 wt% to about 35 wt%, from about 10 wt% to about 35 wt%, from about 15 wt% to about 35 wt%, from about 20 wt% to about 35 wt%, from about 25 wt% to about 35 wt%, from about 30 wt% to about 35 wt%, from about 5 wt% to about 30 wt%, from about 10 wt% to about 30 wt%, from about 15 wt% to about 30 wt%, from about 20 wt% to about 30 wt%, from about 25 wt% to about 30 wt%, from about 5 wt% to about 25 wt%, from about 10 wt% to about 25 wt%, from about 15 wt% to about 25 wt%, from about 20 wt% to about 25 wt%, from about 5 wt% to about 20 wt%, from about 10 wt% to about 20 wt%, from about 15 wt% to about 20 wt%, from about 5 wt% to about 15 wt%, from about 10 wt% to about 15 wt%, from about 5 wt% to about 10 wt%, about 5 wt%, about 10 wt%, about 15 wt%, about 20 wt%, about 25 wt%, about 30 wt%, about 35 wt%, about 40 wt%, about 45 wt%, about 50

wt%, or any range or value therebetween. In a preferred embodiment, the supplementary cementitious material is present in an amount of about 5 wt% to about 50 wt% by dry weight based on the total dry weight of the cementitious composition of the present invention. In other preferred embodiments, the supplementary cementitious material is present in an amount of about 5 wt% to about 30 wt% by dry weight based on the total dry weight of the cementitious composition of the present invention. In yet other preferred embodiments, the supplementary cementitious material is present in an amount of about 20 wt% to about 30 wt% by dry weight based on the total dry weight of the cementitious composition of the present invention. In a further preferred embodiment, the supplementary cementitious material is present in an amount of about 30 wt% by dry weight based on the total dry weight of the cementitious composition of the present invention.

The amount of OPC replaced by supplementary cementitious composition may be dependent on the amount of kaolinite content in the clay material. Generally, the higher the amount of kaolinite in the clay material, the higher amount of OPC may be replaced by supplementary cementitious composition. The inventors have surprisingly found sites in Singapore where the kaolinite content of marine clay is as high as 61% (Lorong Halus). Hence, when marine clay from such regions with high kaolinite content is used (for example, 50% and higher), the cementitious compositions of the present invention may advantageously have high replacement of OPC, for example, 50% replacement of OPC with supplementary cementitious composition.

As mentioned, the supplementary cementitious material may comprise carbonate material to improve the strength of the final cementitious composition. The carbonate material may be chosen from limestone, calcium magnesium carbonate, calcium carbonate, or mixtures and combinations thereof. In a preferred embodiment, the carbonate material is limestone. In an embodiment, the carbonate material in the cementitious composition of the present invention does not need prior calcination. Further, the carbonate not requiring calcination also helps reduce the carbon footprint of the present invention, while at the same time also reducing energy costs.

The ratio of the calcined clay material to limestone may be based on the stoichiometry of kaolinite in the original clay material in some embodiments. Ideally, not too much limestone is added to not affect the hydration process. The carbonate material may further be present in the cementitious composition of the present invention in various weight ratios relative to the amount of calcined clay material added. In some embodiments, the weight ratio of the calcined clay material to the carbonate material may be at least about 2.5:1, at least about 2.4:1, at least about 2.3:1, at least about 2.2:1, at least about 2.1:1, at least about 2.067:1, at least about 2:1, at least about 1.9:1, at least about 1.8:1, at least about 1.7:1, at least about 1.6:1, at least about 1.5:1, about 2.5:1 to about 1.5:1, about 2.4:1 to about 1.5:1, about 2.3:1 to about 1.5:1, about 2.2:1 to about 1.5:1, about 2.1:1 to about 1.5:1, about 2.067:1 to about 1.5:1, about 2:1 to about 1.5:1, about 1.9:1 to about 1.5:1, about 1.8:1 to about 1.5:1, about 1.7:1 to about 1.5:1, about 1.6:1 to about 1.5:1, about 2.5:1 to about 1.6:1, about 2.4:1 to about 1.6:1, about 2.3:1 to about 1.6:1, about 2.2:1 to about 1.6:1, about

2.1:1 to about 1.6:1, about 2.067:1 to about 1.6:1, about 2:1 to about 1.6:1, about 1.9:1 to about 1.6:1, about 1.8:1 to about 1.6:1, about 1.7:1 to about 1.6:1, about 2.5:1 to about 1.7:1, about 2.4:1 to about 1.7:1, about 2.3:1 to about 1.7:1, about 2.2:1 to about 1.7:1, about 2.1:1 to about 1.7:1, about 2.067:1 to about 1.7:1, about 2:1 to about 1.7:1, about 1.9:1 to about 1.7:1, about 1.8:1 to about 1.7:1, about 2.5:1 to about 1.8:1, about 2.4:1 to about 1.8:1, about 2.3:1 to about 1.8:1, about 2.2:1 to about 1.8:1, about 2.1:1 to about 1.8:1, about 2.067:1 to about 1.8:1, about 2:1 to about 1.8:1, about 1.9:1 to about 1.8:1, about 2.5:1 to about 1.9:1, about 2.4:1 to about 1.9:1, about 2.3:1 to about 1.9:1, about 2.2:1 to about 1.9:1, about 2.1:1 to about 1.9:1, about 2.067:1 to about 1.9:1, about 2:1 to about 1.9:1, about 2.5:1 to about 2:1, about 2.4:1 to about 2:1, about 2.3:1 to about 2:1, about 2.2:1 to about 2:1, about 2.1:1 to about 2:1, about 2.067:1 to about 2:1, about 2.5:1 to about 2.067:1, about 2.4:1 to about 2.067:1, about 2.3:1 to about 2.067:1, about 2.2:1 to about 2.067:1, about 2.1:1 to about 2.067:1, about 2.5:1 to about 2.1:1, about 2.4:1 to about 2.1:1, about 2.3:1 to about 2.1:1, about 2.2:1 to about 2.1:1, about 2.5:1 to about 2.2:1, about 2.4:1 to about 2.2:1, about 2.3:1 to about 2.2:1, about 2.5:1 to about 2.3:1, about 2.4:1 to about 2.3:1, about 2.5:1 to about 2.4:1, about 2.5:1, about 2.4:1, about 2.3:1, about 2.2:1, about 2.1:1, about 2.067:1, about 2:1, about 1.9:1, about 1.8:1, about 1.7:1, about 1.6:1, about 1.5:1, or any ratio or ranges therebetween. In some preferred embodiments, the weight ratio of the calcined clay material to the carbonate material is about 1.5:1 to about 2.5:1. In other preferred embodiments, the weight ratio of the calcined clay material to the carbonate materials about 2:1 to about 2.1:1. In yet other preferred embodiments, the weight ratio of the calcined clay material to the carbonate material is either about 2:1 or about 2.067:1, or about 2.1:1.

The conditions at which cement may be replaced with calcined clay material-containing supplementary cementitious material has not been previously studied with respect to the presence of calcium sulphate (gypsum). The addition of a sulphate material, such as gypsum, is key to producing a cementitious composition with strong compressive strength. The increased demand for sulphate inside the composition is linked to the enhancement of alite reaction due to filler effect and the adsorption of sulphate in C-A-S-H, rather than the aluminate content of the calcined clay. In addition, the reaction rate of tricalcium aluminate (C3A) and the dissolution rate of the sulphate source used are also important to describe the sulphate balance of a cementitious system in general. Moreover, the sulphate content is required to be balanced for the replaced cement portion. Otherwise, this will eventually reduce the setting time of the LC³ binder and hence, the sulphate content is required to be calibrated and the inventors have surprisingly found the optimum amount of gypsum required to obtain a cementitious composition with strong compressive strength. Different sulphate materials may be used, for example, gypsum, bassanite, anhydrite, calcium sulphate, magnesium sulphate, or mixtures and combinations thereof. In a preferred embodiment, the sulphate material is gypsum.

In some embodiments, the sulphate material may be present based on the total dry weight of the supplementary cementitious composition, in an amount of at least about 0.5 wt%, at least about 1 wt%, at least about 1.5 wt%, at least about 2 wt%, at least about 2.5 wt%, at least about 3 wt%, at least about 3.5

wt%, at least about 4 wt%, at least about 4.5 wt%, at least about 5 wt%, at least about 5.5 wt%, at least about 6 wt%, at least about 6.5 wt%, at least about 7 wt%, at least about 7.5 wt%, at least about 8 wt%, at least about 8.5 wt%, at least about 9 wt%, at least about 9.5 wt%, at least about 10 wt%, at least about 10.5 wt%, at least about 11 wt%, at least about 11.5 wt%, at least about 12 wt%, at least about 12.5 wt%, at least about 13 wt%, at least about 13.5 wt%, at least about 14 wt%, at least about 14.5 wt%, or at least about 15 wt%. The cementitious composition may contain about 0.5 wt% to about 15 wt% by dry weight based on the total dry weight of supplementary cementitious composition, or about 1 wt% to about 15 wt%, about 1.5 wt% to about 15 wt%, about 2 wt% to about 15 wt%, about 2.5 wt% to about 15 wt%, about 3 wt% to about 15 wt%, about 3.5 wt% to about 15 wt%, about 4 wt% to about 15 wt%, about 4.5 wt% to about 15 wt%, about 5 wt% to about 15 wt%, about 5.5 wt% to about 15 wt%, about 6 wt% to about 15 wt%, about 6.5 wt% to about 15 wt%, about 7 wt% to about 15 wt%, about 7.5 wt% to about 15 wt%, about 8 wt% to about 15 wt%, about 8.5 wt% to about 15 wt%, about 9 wt% to about 15 wt%, about 9.5 wt% to about 15 wt%, about 10 wt% to about 15 wt%, about 10.5 wt% to about 15 wt%, about 11 wt% to about 15 wt%, about 11.5 wt% to about 15 wt%, about 12 wt% to about 15 wt%, about 12.5 wt% to about 15 wt%, about 13 wt% to about 15 wt%, about 13.5 wt% to about 15 wt%, about 14 wt% to about 15 wt%, about 14.5 wt% to about 15 wt%, about 1 wt% to about 15 wt%, or about 0.5 wt%, about 1 wt%, about 1.5 wt%, about 2 wt%, about 2.5 wt%, about 3 wt%, about 3.5 wt%, about 4 wt%, about 4.5 wt%, about 6 wt%, about 6.5 wt%, about 7 wt%, about 7.5 wt%, about 8 wt%, about 8.5 wt%, about 9 wt%, about 10 wt%, about 10.5 wt%, about 11 wt%, about 11.5 wt%, about 12 wt%, about 12.5 wt%, about 13 wt%, about 13.5 wt%, about 14 wt%, about 14.5 wt%, about 15 wt%, or any range or value therebetween.

In some other embodiments, the sulphate material may also be added to the cementitious composition in a weight ratio relative to the calcined clay material. In some embodiments, the weight ratio of the calcined clay material to the sulphate material is at least about 8.5:1, at least about 8.25:1, at least about 8:1, at least about 7.75:1, at least about 7.5:1, at least about 7.25:1, at least about 7:1, at least about 6.75:1, at least about 6.5:1, about 8.5:1 to about 6.5:1, about 8.25:1 to about 6.5:1, about 8:1 to about 6.5:1, about 7.75:1 to about 6.5:1, about 7.5:1 to about 6.5:1, about 7.25:1 to about 6.5:1, about 7:1 to about 6.5:1, about 6.75:1 to about 6.5:1, about 8.5:1 to about 6.75:1, about 8.25:1 to about 6.75:1, about 8:1 to about 6.75:1, about 7.75:1 to about 6.75:1, about 7.5:1 to about 6.75:1, about 7.25:1 to about 6.75:1, about 7:1 to about 6.75:1, about 8.5:1 to about 7:1, about 8.25:1 to about 7:1, about 8:1 to about 7:1, about 7.75:1 to about 7:1, about 7.5:1 to about 7:1, about 7.25:1 to about 7:1, about 8.5:1 to about 7.25:1, about 8.25:1 to about 7.25:1, about 8:1 to about 7.25:1, about 7.75:1 to about 7.25:1, about 7.5:1 to about 7.25:1, about 8.5:1 to about 7.5:1, about 8.25:1 to about 7.5:1, about 8:1 to about 7.5:1, about 7.75:1 to about 7.5:1, about 8.5:1 to about 7.75:1, about 8.25:1 to about 7.75:1, about 8:1 to about 7.75:1, about 8.5:1 to about 8:1, about 8.25:1 to about 8:1, about 8.5:1 to about 8.25:1, about 8.5:1, about 8.25:1, about 8:1, about 7.75:1, about 7.5:1, about 7.25:1, about 7:1, about 6.75:1, about 6.5:1, or any values or ranges therebetween. In some preferred embodiments, the weight ratio of calcined clay material to the sulphate material is about

7:1 to about 8:1. In a further preferred embodiment, the weight ratio of calcined clay material to the sulphate material is about 7.75:1.

In an embodiment, the ratio of calcined marine clay : carbonate material : sulfate material is about 30:15:5 (60:30:10), or about 31:15:4 (62:30:8). In an embodiment, the ratio of calcined marine clay : limestone : gypsum is about 30:15:5, or about 31:15:4.

Various additional materials may be added to the cementitious composition to form other construction materials. For example, sand and water may be added to the cementitious composition of the present invention to form mortar; while sand, aggregate/gravel and water may be added to the cementitious composition to form concrete.

In a preferred embodiment, the present disclosure provides for a cementitious composition, comprising:

- (a) Portland cement clinker in an amount of from about 70 wt% to 80 wt% by dry weight based on the total dry weight of the cementitious composition; and
- (b) supplementary cementitious material in an amount from about 20 wt% to about 30 wt% by dry weight based on the total dry weight of the cementitious composition,
 - wherein the supplementary cementitious material comprises:
 - (i) calcined clay material produced from heating a clay material at a maximum temperature of about 700 °C to about 900 °C, wherein the clay material contains at least about 25 wt% to about 35 wt% kaolinite;
 - (ii) limestone; and
 - (iii) gypsum,

wherein the weight ratio of the calcined clay material to the limestone is about 2:1 to about 2.1:1.

In another preferred embodiment, the present disclosure provides for a cementitious composition comprising:

- (a) Portland cement clinker in an amount of from about 70 wt% to 80 wt% by dry weight based on the total dry weight of the cementitious composition; and
- (b) supplementary cementitious material in an amount from about 20 wt% to about 30 wt% by dry weight based on the total dry weight of the cementitious composition,
 - wherein the supplementary cementitious material comprises:
 - (i) calcined clay material produced from heating a clay material at a maximum temperature of between about 700 °C to about 900 °C;
 - (ii) carbonate material selected from the group consisting of limestone, calcium magnesium carbonate, and mixtures thereof; and

- (iii) sulphate material selected from the group consisting of gypsum, bassanite, anhydrite, and mixtures thereof,

wherein the weight ratio of the calcined clay material to the carbonate material is about 2:1.

5 The present disclosure also provides for a method of producing a cementitious composition, comprising:

- (a) heating a clay material at a maximum temperature of about 700 °C to about 900 °C to form a calcined clay material;
- (b) mixing the calcined clay material with a carbonate material selected from the group consisting of limestone, calcium magnesium carbonate, and mixtures thereof, and a sulphate material
10 selected from the group consisting of gypsum, bassanite, anhydrite, and mixtures thereof to form a supplementary cementitious mixture;
- (c) blending the supplementary cementitious mixture with Portland cement clinker,

wherein:

15 the Portland cement clinker is in an amount of from about 70 wt% to 95 wt% by dry weight based on the total dry weight of the cementitious composition;

the supplementary cementitious material in an amount from about 5 wt% to about 30 wt% by dry weight based on the total dry weight of the cementitious composition;

the weight ratio of the calcined clay material to the carbonate material is about 1.5:1 to about 2.1:1.

20 The present invention provides for a method of producing a cementitious composition comprising a step of mixing the calcined clay material with a carbonate material and a sulphate material to form a supplementary cementitious material (SCM). The carbonate material may be chosen from limestone, calcium carbonate, calcium magnesium carbonate, and mixtures and combinations thereof. The sulphate material may also be selected from the group consisting of gypsum, bassanite, anhydrite, or mixtures and combinations thereof.

25 The present invention provides for a method of activating the kaolinite in clay material by heating the same clay material at an elevated temperature to convert to the kaolinite to metakaolin. In some embodiments, the method provides for a step of heating a clay material at a maximum temperature to form a calcined clay material, wherein the maximum temperature may be at least about 500 °C, at least about 550 °C, at least about 600 °C, at least about 650 °C, at least about 700 °C, at least about 750 °C, at least
30 about 800 °C, at least about 850 °C, at least about 900 °C, at least about 950 °C, at least about 1000 °C, at least about 1050 °C, at least about 1100 °C, at least about 1200 °C, about 500 °C to about 1200 °C, about 550 °C to about 1200 °C, about 600 °C to about 1200 °C, about 650 °C to about 1200 °C, about 700 °C to

about 1200 °C, about 750 °C to about 1200 °C, about 800 °C to about 1200 °C, about 850 °C to about 1200 °C, about 900 °C to about 1200 °C, about 950 °C to about 1200 °C, about 1000 °C to about 1200 °C, about 1050 °C to about 1200 °C, about 1100 °C to about 1200 °C, about 500 °C to about 1100 °C, about 550 °C to about 1100 °C, about 600 °C to about 1100 °C, about 650 °C to about 1100 °C, about 700 °C to about 1100 °C, about 750 °C to about 1100 °C, about 800 °C to about 1100 °C, about 850 °C to about 1100 °C, about 900 °C to about 1100 °C, about 950 °C to about 1100 °C, about 1000 °C to about 1100 °C, about 1050 °C to about 1100 °C, about 500 °C to about 1050 °C, about 550 °C to about 1050 °C, about 600 °C to about 1050 °C, about 650 °C to about 1050 °C, about 700 °C to about 1050 °C, about 750 °C to about 1050 °C, about 800 °C to about 1050 °C, about 850 °C to about 1050 °C, about 900 °C to about 1050 °C, about 950 °C to about 1050 °C, about 1000 °C to about 1050 °C, about 500 °C to about 1000 °C, about 550 °C to about 1000 °C, about 600 °C to about 1000 °C, about 650 °C to about 1000 °C, about 700 °C to about 1000 °C, about 750 °C to about 1000 °C, about 800 °C to about 1000 °C, about 850 °C to about 1000 °C, about 900 °C to about 1000 °C, about 950 °C to about 1000 °C, about 500 °C to about 950 °C, about 550 °C to about 950 °C, about 600 °C to about 950 °C, about 650 °C to about 950 °C, about 700 °C to about 950 °C, about 750 °C to about 950 °C, about 800 °C to about 950 °C, about 850 °C to about 950 °C, about 900 °C to about 950 °C, about 500 °C to about 900 °C, about 550 °C to about 900 °C, about 600 °C to about 900 °C, about 650 °C to about 900 °C, about 700 °C to about 900 °C, about 750 °C to about 900 °C, about 800 °C to about 900 °C, about 850 °C to about 900 °C, about 500 °C to about 850 °C, about 550 °C to about 850 °C, about 600 °C to about 850 °C, about 650 °C to about 850 °C, about 700 °C to about 850 °C, about 750 °C to about 850 °C, about 800 °C to about 850 °C, about 500 °C to about 800 °C, about 550 °C to about 800 °C, about 600 °C to about 800 °C, about 650 °C to about 800 °C, about 700 °C to about 800 °C, about 750 °C to about 800 °C, about 500 °C to about 750 °C, about 550 °C to about 750 °C, about 600 °C to about 750 °C, about 650 °C to about 750 °C, about 700 °C to about 750 °C, about 500 °C to about 700 °C, about 550 °C to about 700 °C, about 600 °C to about 700 °C, about 650 °C to about 700 °C, about 500 °C to about 650 °C, about 550 °C to about 650 °C, about 600 °C to about 650 °C, about 500 °C to about 600 °C, about 550 °C to about 600 °C, about 500 °C to about 550 °C, about 500 °C, about 550 °C, about 600 °C, about 650 °C, about 700 °C, about 750 °C, about 800 °C, about 850 °C, about 900 °C, about 950 °C, about 1000 °C, about 1050 °C, about 1100 °C, about 1200 °C, or any range of value therebetween. In some preferred embodiments, the calcination temperature is between about 700 °C to about 900 °C. In a further preferred embodiment, the maximum temperature is about 900 °C.

The method of producing a cementitious composition of the present invention involves a step of heating clay material at a steady rate to reach a maximum temperature, after which the clay material is then held at the maximum temperature for a minimum duration to form a calcined clay material. In some embodiments, the rate at which the calcined clay is heated up to a maximum temperature may be at least about 2 °C per minute, at least about 4 °C per minute, at least about 5 °C per minute, at least about 6 °C per minute, at least about 8 °C per minute, at least about 10 °C per minute, at least about 12 °C per minute, at least about 14 °C per minute, at least about 15 °C per minute, at least about 16 °C per minute, at least about

18 °C per minute, at least about 20 °C per minute, about 2 °C per minute to about 20 °C per minute, about 4 °C per minute to about 20 °C per minute, about 5 °C per minute to about 20 °C per minute, about 6 °C per minute to about 20 °C per minute, about 8 °C per minute to about 20 °C per minute, about 10 °C per minute to about 20 °C per minute, about 12 °C per minute to about 20 °C per minute, about 14 °C per minute to about 20 °C per minute, about 15 °C per minute to about 20 °C per minute, about 16 °C per minute to about 20 °C per minute, about 18 °C per minute to about 20 °C per minute, about 2 °C per minute to about 18 °C per minute, about 4 °C per minute to about 18 °C per minute, about 5 °C per minute to about 18 °C per minute, about 6 °C per minute to about 18 °C per minute, about 8 °C per minute to about 18 °C per minute, about 10 °C per minute to about 18 °C per minute, about 12 °C per minute to about 18 °C per minute, about 14 °C per minute to about 18 °C per minute, about 15 °C per minute to about 18 °C per minute, about 16 °C per minute to about 18 °C per minute, about 2 °C per minute to about 16 °C per minute, about 4 °C per minute to about 16 °C per minute, about 5 °C per minute to about 16 °C per minute, about 6 °C per minute to about 16 °C per minute, about 8 °C per minute to about 16 °C per minute, about 10 °C per minute to about 16 °C per minute, about 12 °C per minute to about 16 °C per minute, about 14 °C per minute to about 16 °C per minute, about 15 °C per minute to about 16 °C per minute, about 2 °C per minute to about 15 °C per minute, about 4 °C per minute to about 15 °C per minute, about 5 °C per minute to about 15 °C per minute, about 6 °C per minute to about 15 °C per minute, about 8 °C per minute to about 15 °C per minute, about 10 °C per minute to about 15 °C per minute, about 12 °C per minute to about 15 °C per minute, about 14 °C per minute to about 15 °C per minute, about 2 °C per minute to about 14 °C per minute, about 4 °C per minute to about 14 °C per minute, about 5 °C per minute to about 14 °C per minute, about 6 °C per minute to about 14 °C per minute, about 8 °C per minute to about 14 °C per minute, about 10 °C per minute to about 14 °C per minute, about 12 °C per minute to about 14 °C per minute, about 2 °C per minute to about 12 °C per minute, about 4 °C per minute to about 12 °C per minute, about 5 °C per minute to about 12 °C per minute, about 6 °C per minute to about 12 °C per minute, about 8 °C per minute to about 12 °C per minute, about 10 °C per minute to about 12 °C per minute, about 2 °C per minute to about 10 °C per minute, about 4 °C per minute to about 10 °C per minute, about 5 °C per minute to about 10 °C per minute, about 6 °C per minute to about 10 °C per minute, about 8 °C per minute to about 10 °C per minute, about 2 °C per minute to about 8 °C per minute, about 4 °C per minute to about 8 °C per minute, about 5 °C per minute to about 8 °C per minute, about 6 °C per minute to about 8 °C per minute, about 2 °C per minute to about 6 °C per minute, about 4 °C per minute to about 6 °C per minute, about 5 °C per minute to about 6 °C per minute, about 2 °C per minute to about 5 °C per minute, about 4 °C per minute to about 5 °C per minute, about 2 °C per minute to about 4 °C per minute, about 2 °C per minute, about 4 °C per minute, about 5 °C per minute, about 6 °C per minute, about 8 °C per minute, about 10 °C per minute, about 12 °C per minute, about 14 °C per minute, about 15 °C per minute, about 16 °C per minute, about 18 °C per minute, about 20 °C per minute, or any ranges or values therebetween. In a preferred embodiment, the method of producing a cementitious composition of the present invention comprises a step of heating a clay material to a maximum temperature disclosed herein, wherein the clay material is initially heated up

at a rate of about 5 °C per minute to about 15 °C per minute to reach the maximum temperature. In a further preferred embodiment, the calcined clay is heated up at a rate of about 10 °C per minute to reach the maximum temperature.

The method of producing the cementitious composition of the present invention may also comprise a step of heating the clay material at a maximum temperature to form calcined clay material, wherein the maximum temperature is to be maintained for a minimum duration to ensure complete conversion of the kaolinite in the clay material to the active metakaolin form. In some embodiments, the maximum temperature is maintained for at least about 1 hour, at least about 1.25 hours, at least about 1.5 hours, at least about 1.75 hours, at least about 2 hours, at least about 2.25 hours, at least about 2.5 hours, at least about 2.75 hours, at least about 3 hours, at least about 3.25 hours, at least about 3.5 hours, at least about 4 hours, about 1 hour to about 4 hours, about 1.25 hours to about 4 hours, about 1.5 hours to about 4 hours, about 1.75 hours to about 4 hours, about 2 hours to about 4 hours, about 2.25 hours to about 4 hours, about 2.5 hours to about 4 hours, about 2.75 hours to about 4 hours, about 3 hours to about 4 hours, about 3.25 hours to about 4 hours, about 3.5 hours to about 4 hours, about 1 hour to about 3.5 hours, about 1.25 hours to about 3.5 hours, about 1.5 hours to about 3.5 hours, about 1.75 hours to about 3.5 hours, about 2 hours to about 3.5 hours, about 2.25 hours to about 3.5 hours, about 2.5 hours to about 3.5 hours, about 2.75 hours to about 3.5 hours, about 3 hours to about 3.5 hours, about 3.25 hours to about 3.5 hours, about 1 hour to about 3.25 hours, about 1.25 hours to about 3.25 hours, about 1.5 hours to about 3.25 hours, about 1.75 hours to about 3.25 hours, about 2 hours to about 3.25 hours, about 2.25 hours to about 3.25 hours, about 2.5 hours to about 3.25 hours, about 2.75 hours to about 3.25 hours, about 3 hours to about 3.25 hours, about 1 hour to about 3 hours, about 1.25 hours to about 3 hours, about 1.5 hours to about 3 hours, about 1.75 hours to about 3 hours, about 2 hours to about 3 hours, about 2.25 hours to about 3 hours, about 2.5 hours to about 3 hours, about 2.75 hours to about 3 hours, about 1 hour to about 2.75 hours, about 1.25 hours to about 2.75 hours, about 1.5 hours to about 2.75 hours, about 1.75 hours to about 2.75 hours, about 2 hours to about 2.75 hours, about 2.25 hours to about 2.75 hours, about 2.5 hours to about 2.75 hours, about 1 hour to about 2.5 hours, about 1.25 hours to about 2.5 hours, about 1.5 hours to about 2.5 hours, about 1.75 hours to about 2.5 hours, about 2 hours to about 2.5 hours, about 2.25 hours to about 2.5 hours, about 1 hour to about 2.25 hours, about 1.25 hours to about 2.25 hours, about 1.5 hours to about 2.25 hours, about 1.75 hours to about 2.25 hours, about 2 hours to about 2.25 hours, about 1 hour to about 2 hours, about 1.25 hours to about 2 hours, about 1.5 hours to about 2 hours, about 1.75 hours to about 2 hours, about 1 hour to about 1.75 hours, about 1.25 hours to about 1.75 hours, about 1.5 hours to about 1.75 hours, about 1 hour to about 1.5 hours, about 1.25 hours to about 1.5 hours, about 1 hour to about 1.25 hours, about 1 hour, about 1.25 hours, about 1.5 hours, about 1.75 hours, about 2 hours, about 2.25 hours, about 2.5 hours, about 2.75 hours, about 3 hours, about 3.25 hours, about 3.5 hours, about 4 hours, or any ranges or values therebetween. In a preferred embodiment, the method of producing a cementitious composition of the present invention comprises heating a clay material at a maximum temperature disclosed herein,

wherein the maximum temperature is maintained for at least 1 hour. In yet a preferred embodiment, the maximum temperature is maintained for at least 2 hours.

In some embodiments, the method of producing a cementitious composition of the present invention comprises a step of heating a clay material at a maximum temperature disclosed herein to form a calcined clay material, wherein the clay material is heated at a rate of about 5 °C to about 15 °C per minute up to a maximum temperature of about 500 °C to about 900 °C, and the maximum temperature is maintained for at least 1 hour. In some embodiments, the clay material is heated at a rate of about 10 °C per minute up to a maximum temperature of about 500 °C to about 900 °C, and the maximum temperature is maintained for at least 1 hour. In some embodiments, the clay material is heated at a rate of about 5 °C to about 15 °C per minute up to a maximum temperature of about 700 °C to about 900 °C, and the maximum temperature is maintained for at least 1 hour. In some embodiments, the clay material is heated at a rate of about 10 °C per minute up to a maximum temperature of about 700 °C to about 900 °C, and the maximum temperature is maintained for at least 1 hour. In some embodiments, the clay material is heated at a rate of about 5 °C to about 15 °C per minute up to a maximum temperature of about 900 °C, and the maximum temperature is maintained for at least 1 hour. In some embodiments, the clay material is heated at a rate of about 10 °C per minute up to a maximum temperature of about 900 °C, and the maximum temperature is maintained for at least 1 hour. In some embodiments, the clay material is heated at a rate of about 5 °C to about 15 °C per minute up to a maximum temperature of about 500 °C to about 900 °C, and the maximum temperature is maintained for at least 2 hours. In some embodiments, the clay material is heated at a rate of about 10 °C per minute up to a maximum temperature of about 500 °C to about 900 °C, and the maximum temperature is maintained for at least 2 hours. In some embodiments, the clay material is heated at a rate of about 5 °C to about 15 °C per minute up to a maximum temperature of about 700 °C to about 900 °C, and the maximum temperature is maintained for at least 2 hours. In some embodiments, the clay material is heated at a rate of about 10 °C per minute up to a maximum temperature of about 700 °C to about 900 °C, and the maximum temperature is maintained for at least 2 hours. In some embodiments, the clay material is heated at a rate of about 5 °C to about 15 °C per minute up to a maximum temperature of about 900 °C, and the maximum temperature is maintained for at least 2 hours. In some embodiments, the clay material is heated at a rate of about 10 °C per minute up to a maximum temperature of about 900 °C, and the maximum temperature is maintained for at least 2 hours.

The present invention also provides a method for producing a cementitious composition, comprising a step of mixing the supplementary cementitious material with Portland cement clinker. Accordingly, in the method disclosed herein, the Portland cement clinker may be present, by dry weight based on the total dry weight of the cementitious composition, in at least about 50 wt%, at least about 55 wt%, at least about 60 wt%, at least about 65 wt%, at least about 70 wt%, at least about 75 wt%, at least about 80 wt%, at least about 85 wt%, at least about 90 wt%, at least about 95 wt%, from about 50 wt% to about 95 wt%, from about 55 wt% to about 95 wt%, from about 60 wt% to about 95 wt%, from about 65

wt% to about 95 wt%, from about 70 wt% to about 95 wt%, from about 75 wt% to about 95 wt%, from about 80 wt% to about 95 wt%, from about 85 wt% to about 95 wt%, from about 90 wt% to about 95 wt%, from about 50 wt% to about 90 wt%, from about 55 wt% to about 90 wt%, from about 60 wt% to about 90 wt%, from about 65 wt% to about 90 wt%, from about 70 wt% to about 90 wt%, from about 75 wt% to about 90 wt%, from about 80 wt% to about 90 wt%, from about 85 wt% to about 90 wt%, from about 50 wt% to about 85 wt%, from about 55 wt% to about 85 wt%, from about 60 wt% to about 85 wt%, from about 65 wt% to about 85 wt%, from about 70 wt% to about 85 wt%, from about 75 wt% to about 85 wt%, from about 80 wt% to about 85 wt%, from about 50 wt% to about 80 wt%, from about 55 wt% to about 80 wt%, from about 60 wt% to about 80 wt%, from about 65 wt% to about 80 wt%, from about 70 wt% to about 80 wt%, from about 75 wt% to about 80 wt%, from about 50 wt% to about 75 wt%, from about 55 wt% to about 75 wt%, from about 60 wt% to about 75 wt%, from about 65 wt% to about 75 wt%, from about 70 wt% to about 75 wt%, from about 50 wt% to about 70 wt%, from about 55 wt% to about 70 wt%, from about 60 wt% to about 70 wt%, from about 65 wt% to about 70 wt%, from about 50 wt% to about 65 wt%, from about 55 wt% to about 65 wt%, from about 60 wt% to about 65 wt%, from about 50 wt% to about 60 wt%, from about 55 wt% to about 60 wt%, from about 50 wt% to about 55 wt%, about 50 wt%, about 55 wt%, about 60 wt%, about 65 wt%, about 70 wt%, about 75 wt%, about 80 wt%, about 85 wt%, about 90 wt%, about 95 wt%, or any range or value therebetween. In a preferred embodiment, the Portland cement clinker is present in about 50 wt% to about 95 wt% by dry weight of the total dry weight of the cementitious composition of the present invention. In yet another preferred embodiment the Portland cement clinker is present in about 70 wt% to about 95 wt% by dry weight of the total dry weight of the cementitious composition of the present invention. In a further preferred embodiment, the Portland cement clinker is present in about 70 wt% to about 80 wt% by dry weight of the total dry weight of the cementitious composition of the present invention. In yet another preferred embodiment, the Portland cement clinker is present in about 70 wt% by dry weight of the total dry weight of the cementitious composition of the present invention.

Further, the present invention also provides a method for producing a cementitious composition, wherein the supplementary cementitious material is present in the final cementitious composition in various percentages, in at least about 5 wt%, at least about 10 wt%, at least about 15 wt%, at least about 20 wt%, at least about 25 wt%, at least about 30 wt%, at least about 35 wt%, at least about 40 wt%, at least about 45 wt%, at least about 50 wt%, from about 5 wt% to about 50 wt%, from about 10 wt% to about 50 wt%, from about 15 wt% to about 50 wt%, from about 20 wt% to about 50 wt%, from about 25 wt% to about 50 wt%, from about 30 wt% to about 50 wt%, from about 35 wt% to about 50 wt%, from about 40 wt% to about 50 wt%, from about 45 wt% to about 50 wt%, from about 5 wt% to about 45 wt%, from about 10 wt% to about 45 wt%, from about 15 wt% to about 45 wt%, from about 20 wt% to about 45 wt%, from about 25 wt% to about 45 wt%, from about 30 wt% to about 45 wt%, from about 35 wt% to about 45 wt%, from about 40 wt% to about 45 wt%, from about 5 wt% to about 40 wt%, from about 10 wt% to about 40 wt%, from about 15 wt% to about 40 wt%, from about 20 wt% to about 40 wt%, from about 25

wt% to about 40 wt%, from about 30 wt% to about 40 wt%, from about 35 wt% to about 40 wt%, from about 5 wt% to about 35 wt%, from about 10 wt% to about 35 wt%, from about 15 wt% to about 35 wt%, from about 20 wt% to about 35 wt%, from about 25 wt% to about 35 wt%, from about 30 wt% to about 35 wt%, from about 5 wt% to about 30 wt%, from about 10 wt% to about 30 wt%, from about 15 wt% to about 30 wt%, from about 20 wt% to about 30 wt%, from about 25 wt% to about 30 wt%, from about 5 wt% to about 25 wt%, from about 10 wt% to about 25 wt%, from about 15 wt% to about 25 wt%, from about 20 wt% to about 25 wt%, from about 5 wt% to about 20 wt%, from about 10 wt% to about 20 wt%, from about 15 wt% to about 20 wt%, from about 5 wt% to about 15 wt%, from about 10 wt% to about 15 wt%, from about 5 wt% to about 10 wt%, about 5 wt%, about 10 wt%, about 15 wt%, about 20 wt%, about 25 wt%, about 30 wt%, about 35 wt%, about 40 wt%, about 45 wt%, about 50 wt%, or any range or value therebetween. In a preferred embodiment, the method of producing a cementitious composition comprises a step blending step of the supplementary cementitious material with Portland cement clinker, wherein the supplementary cementitious material is present in about 5 wt% to about 50 wt% by dry weight based on the total dry weight of the cementitious composition of the present invention. In other preferred embodiments, the supplementary cementitious material is present in about 5 wt% to about 30 wt% by dry weight based on the total dry weight of the cementitious composition of the present invention. In yet other preferred embodiments, the supplementary cementitious material is present in about 20 wt% to about 30 wt% by dry weight based on the total dry weight of the cementitious composition of the present invention. In a further preferred embodiment, the supplementary cementitious material is present in about 30 wt% by dry weight based on the total dry weight of the cementitious composition of the present invention.

The method of producing the cementitious composition of the present invention involves the inventive step of replacing Portland cement clinker with supplementary cementitious material, wherein the cementitious material comprises calcined clay material. Accordingly, the calcined clay material may be formed from the heating of raw kaolinite-containing clay material at a maximum temperature for a minimum duration to form the calcined clay material. In some embodiments, the clay material contains a desirable amount of kaolinite by weight of the total clay material, for example, at least about 15 wt%, at least about 20 wt%, at least about 25 wt%, at least about 29 wt%, at least about 30 wt%, at least about 35 wt%, at least about 40 wt%, at least about 45 wt%, at least about 50 wt%, at least about 61 wt%, at least about 70 wt%, at least about 80 wt%, at least about 90 wt%, about 15 wt% to about 90 wt%, about 20 wt% to about 90 wt%, about 25 wt% to about 90 wt%, about 29 wt% to about 90 wt%, about 30 wt% to about 90 wt%, about 35 wt% to about 90 wt%, about 40 wt% to about 90 wt%, about 45 wt% to about 90 wt%, about 50 wt% to about 90 wt%, about 61 wt% to about 90 wt%, about 70 wt% to about 90 wt%, about 80 wt% to about 90 wt%, about 15 wt% to about 80 wt%, about 20 wt% to about 80 wt%, about 25 wt% to about 80 wt%, about 29 wt% to about 80 wt%, about 30 wt% to about 80 wt%, about 35 wt% to about 80 wt%, about 40 wt% to about 80 wt%, about 45 wt% to about 80 wt%, about 50 wt% to about 80 wt%, about 61 wt% to about 80 wt%, about 70 wt% to about 80 wt%, about 15 wt% to about 70 wt%, about 20 wt% to about 70 wt%, about 25 wt% to about 70 wt%, about 29 wt% to about 70 wt%, about 30 wt% to

about 70 wt%, about 35 wt% to about 70 wt%, about 40 wt% to about 70 wt%, about 45 wt% to about 70 wt%, about 50 wt% to about 70 wt%, about 61 wt% to about 70 wt%, about 15 wt% to about 61 wt%, about 20 wt% to about 61 wt%, about 25 wt% to about 61 wt%, about 29 wt% to about 61 wt%, about 30 wt% to about 61 wt%, about 35 wt% to about 61 wt%, about 40 wt% to about 61 wt%, about 45 wt% to about 61 wt%, about 50 wt% to about 61 wt%, about 15 wt% to about 50 wt%, about 20 wt% to about 50 wt%, about 25 wt% to about 50 wt%, about 29 wt% to about 50 wt%, about 30 wt% to about 50 wt%, about 35 wt% to about 50 wt%, about 40 wt% to about 50 wt%, about 45 wt% to about 50 wt%, about 15 wt% to about 45 wt%, about 20 wt% to about 45 wt%, about 25 wt% to about 45 wt%, about 29 wt% to about 45 wt%, about 30 wt% to about 45 wt%, about 35 wt% to about 45 wt%, about 40 wt% to about 45 wt%, about 15 wt% to about 40 wt%, about 20 wt% to about 40 wt%, about 25 wt% to about 40 wt%, about 29 wt% to about 40 wt%, about 30 wt% to about 40 wt%, about 35 wt% to about 40 wt%, about 15 wt% to about 35 wt%, about 20 wt% to about 35 wt%, about 25 wt% to about 35 wt%, about 29 wt% to about 35 wt%, about 30 wt% to about 35 wt%, about 15 wt% to about 30 wt%, about 20 wt% to about 30 wt%, about 25 wt% to about 30 wt%, about 29 wt% to about 30 wt%, about 15 wt% to about 29 wt%, about 20 wt% to about 29 wt%, about 25 wt% to about 29 wt%, about 15 wt% to about 25 wt%, about 20 wt% to about 25 wt%, about 15 wt%, about 20 wt%, about 25 wt%, about 29 wt%, about 30 wt%, about 35 wt%, about 40 wt%, about 45 wt%, about 50 wt%, about 61 wt%, about 70 wt%, about 80 wt%, about 90 wt%, or any ranges or values therebetween. In some preferred embodiments, the method of producing a cementitious composition comprises a step of heating a clay material at a maximum temperature to form a calcined clay material, wherein the clay material comprises at least about 25 wt% kaolinite. In some other preferred embodiments, the clay material comprises about 61 wt% kaolinite. In some further preferred embodiments, the clay material comprises about 25 wt% to about 35 wt% kaolinite. In yet another further preferred embodiment, the clay material comprises about 29 wt% kaolinite.

The method of producing a cementitious composition of the present invention comprises a step of mixing the calcined clay material with a carbonate material. Accordingly, the weight ratio of the calcined clay material to the carbonate material may be at least about 2.5:1, at least about 2.4:1, at least about 2.3:1, at least about 2.2:1, at least about 2.1:1, at least about 2.067:1, at least about 2:1, at least about 1.9:1, at least about 1.8:1, at least about 1.7:1, at least about 1.6:1, at least about 1.5:1, about 2.5:1 to about 1.5:1, about 2.4:1 to about 1.5:1, about 2.3:1 to about 1.5:1, about 2.2:1 to about 1.5:1, about 2.1:1 to about 1.5:1, about 2.067:1 to about 1.5:1, about 2:1 to about 1.5:1, about 1.9:1 to about 1.5:1, about 1.8:1 to about 1.5:1, about 1.7:1 to about 1.5:1, about 1.6:1 to about 1.5:1, about 2.5:1 to about 1.6:1, about 2.4:1 to about 1.6:1, about 2.3:1 to about 1.6:1, about 2.2:1 to about 1.6:1, about 2.1:1 to about 1.6:1, about 2.067:1 to about 1.6:1, about 2:1 to about 1.6:1, about 1.9:1 to about 1.6:1, about 1.8:1 to about 1.6:1, about 1.7:1 to about 1.6:1, about 2.5:1 to about 1.7:1, about 2.4:1 to about 1.7:1, about 2.3:1 to about 1.7:1, about 2.2:1 to about 1.7:1, about 2.1:1 to about 1.7:1, about 2.067:1 to about 1.7:1, about 2:1 to about 1.7:1, about 1.9:1 to about 1.7:1, about 1.8:1 to about 1.7:1, about 2.5:1 to about 1.8:1, about 2.4:1 to about 1.8:1, about 2.3:1 to about 1.8:1, about 2.2:1 to about 1.8:1, about 2.1:1 to about 1.8:1, about 2.067:1 to about 1.8:1, about 2:1 to about

1.8:1, about 1.9:1 to about 1.8:1, about 2.5:1 to about 1.9:1, about 2.4:1 to about 1.9:1, about 2.3:1 to about 1.9:1, about 2.2:1 to about 1.9:1, about 2.1:1 to about 1.9:1, about 2.067:1 to about 1.9:1, about 2:1 to about 1.9:1, about 2.5:1 to about 2:1, about 2.4:1 to about 2:1, about 2.3:1 to about 2:1, about 2.2:1 to about 2:1, about 2.1:1 to about 2:1, about 2.067:1 to about 2:1, about 2.5:1 to about 2.067:1, about 2.4:1 to about 2.067:1, about 2.3:1 to about 2.067:1, about 2.2:1 to about 2.067:1, about 2.1:1 to about 2.067:1, about 2.5:1 to about 2.1:1, about 2.4:1 to about 2.1:1, about 2.3:1 to about 2.1:1, about 2.2:1 to about 2.1:1, about 2.5:1 to about 2.2:1, about 2.4:1 to about 2.2:1, about 2.3:1 to about 2.2:1, about 2.5:1 to about 2.3:1, about 2.4:1 to about 2.3:1, about 2.5:1 to about 2.4:1, about 2.5:1, about 2.4:1, about 2.3:1, about 2.2:1, about 2.1:1, about 2.067:1, about 2:1, about 1.9:1, about 1.8:1, about 1.7:1, about 1.6:1, about 1.5:1, or any ratio or ranges therebetween. In some preferred embodiments, the method of producing a cementitious composition comprises a step of mixing the calcined clay material with a carbonate material, wherein the weight ratio of the calcined clay material to carbonate material is about 1.5:1 to about 2.5:1. In other preferred embodiments, the weight ratio of the calcined clay material is about 2:1 to about 2.1:1. In yet other preferred embodiments, the weight ratio of the calcined clay to the carbonate material is either about 2:1, about 2.067:1, or about 2:1.

In some embodiments, the present disclosure refers to a method of producing a cementitious composition disclosed herein, comprising a step of mixing the calcined clay material with a sulphate material. In some embodiments, the sulphate material may be present based on the total dry weight of the supplementary cementitious material, in an amount of at least at least about 0.5 wt%, at least about 1 wt%, at least about 1.5 wt%, at least about 2 wt%, at least about 2.5 wt%, at least about 3 wt%, at least about 3.5 wt%, at least about 4 wt%, at least about 4.5 wt%, at least about 5 wt%, at least about 5.5 wt%, at least about 6 wt%, at least about 6.5 wt%, at least about 7 wt%, at least about 7.5 wt%, at least about 8 wt%, at least about 8.5 wt%, at least about 9 wt%, at least about 9.5 wt%, at least about 10 wt%, at least about 10.5 wt%, at least about 11 wt%, at least about 11.5 wt%, at least about 12 wt%, at least about 12.5 wt%, at least about 13 wt%, at least about 13.5 wt%, at least about 14 wt%, at least about 14.5 wt%, or at least about 15 wt%. The cementitious composition may contain about 0.5 wt% to about 15 wt% by dry weight based on the total dry weight of supplementary cementitious composition, or about 1 wt% to about 15 wt%, about 1.5 wt% to about 15 wt%, about 2 wt% to about 15 wt%, about 2.5 wt% to about 15 wt%, about 3 wt% to about 15 wt%, about 3.5 wt% to about 15 wt%, about 4 wt% to about 15 wt%, about 4.5 wt% to about 15 wt%, about 5 wt% to about 15 wt%, about 5.5 wt% to about 15 wt%, about 6 wt% to about 15 wt%, about 6.5 wt% to about 15 wt%, about 7 wt% to about 15 wt%, about 7.5 wt% to about 15 wt%, about 8 wt% to about 15 wt%, about 8.5 wt% to about 15 wt%, about 9 wt% to about 15 wt%, about 9.5 wt% to about 15 wt%, about 10 wt% to about 15 wt%, about 10.5 wt% to about 15 wt%, about 11 wt% to about 15 wt%, about 11.5 wt% to about 15 wt%, about 12 wt% to about 15 wt%, about 12.5 wt% to about 15 wt%, about 13 wt% to about 15 wt%, about 13.5 wt% to about 15 wt%, about 14 wt% to about 15 wt%, about 14.5 wt% to about 15 wt%, about 1 wt% to about 15 wt%, or about 0.5 wt%, about 1 wt%, about 1.5 wt%, about 2 wt%, about 2.5 wt%, about 3 wt%, about 3.5 wt%, about 4 wt%, about 4.5 wt%, about 6 wt%,

about 6.5 wt%, about 7 wt%, about 7.5 wt%, about 8 wt%, about 8.5 wt%, about 9 wt%, about 10 wt%, about 10.5 wt%, about 11 wt%, about 11.5 wt%, about 12 wt%, about 12.5 wt%, about 13 wt%, about 13.5 wt%, about 14 wt%, about 14.5 wt%, about 15 wt%, or any range or value therebetween. In some other embodiments, the present disclosure also refers to a method of producing the cementitious composition disclosed herein, comprising a step of mixing the calcined clay material with a sulphate material, wherein the sulphate material is in a weight ratio relative to the calcined clay material, in at least about 8.5:1, at least about 8.25:1, at least about 8:1, at least about 7.75:1, at least about 7.5:1, at least about 7.25:1, at least about 7:1, at least about 6.75:1, at least about 6.5:1, about 8.5:1 to about 6.5:1, about 8.25:1 to about 6.5:1, about 8:1 to about 6.5:1, about 7.75:1 to about 6.5:1, about 7.5:1 to about 6.5:1, about 7.25:1 to about 6.5:1, about 7:1 to about 6.5:1, about 6.75:1 to about 6.5:1, about 8.5:1 to about 6.75:1, about 8.25:1 to about 6.75:1, about 8:1 to about 6.75:1, about 7.75:1 to about 6.75:1, about 7.5:1 to about 6.75:1, about 7.25:1 to about 6.75:1, about 7:1 to about 6.75:1, about 8.5:1 to about 7:1, about 8.25:1 to about 7:1, about 8:1 to about 7:1, about 7.75:1 to about 7:1, about 7.5:1 to about 7:1, about 7.25:1 to about 7:1, about 8.5:1 to about 7.25:1, about 8.25:1 to about 7.25:1, about 8:1 to about 7.25:1, about 7.75:1 to about 7.25:1, about 7.5:1 to about 7.25:1, about 8.5:1 to about 7.5:1, about 8.25:1 to about 7.5:1, about 8:1 to about 7.5:1, about 7.75:1 to about 7.5:1, about 8.5:1 to about 7.75:1, about 8.25:1 to about 7.75:1, about 8:1 to about 7.75:1, about 8.5:1 to about 8:1, about 8.25:1 to about 8:1, about 8.5:1 to about 8.25:1, about 8.5:1, about 8.25:1, about 8:1, about 7.75:1, about 7.5:1, about 7.25:1, about 7:1, about 6.75:1, about 6.5:1, or any values or ranges therebetween. In some preferred embodiments, the present disclosure refers to a method of producing the cementitious composition disclosed herein, comprising a step of mixing the calcined clay material with a sulphate material, wherein the sulphate material is in a weight ratio of calcined clay material to the sulphate material is about 7:1 to about 8:1. In a further preferred embodiment, the present disclosure refers to a method of producing the cementitious composition disclosed herein, comprising a step of mixing the calcined clay material with a sulphate material, wherein the sulphate material is in a weight ratio of calcined clay material to the sulphate material is about 7.75:1.

In some embodiments, the present disclosure refers to a method of producing a cementitious composition disclosed herein, comprising a step of mixing the calcined clay material with a carbonate material selected from the group consisting of limestone, calcium magnesium carbonate, and mixtures thereof, and a sulphate material selected from the group consisting of gypsum, bassanite, anhydrite, and mixtures thereof to form a supplementary cementitious mixture. In some embodiments, the present disclosure refers to a method of producing a cementitious composition disclosed herein, comprising a step of mixing the calcined clay material with a carbonate material, wherein the carbonate material is limestone. In other embodiments, the present disclosure refers to a method of producing a cementitious composition disclosed herein, comprising a step of mixing the calcined clay material with a sulphate material, wherein the sulphate material is gypsum. In some other embodiments, the present disclosure refers to a method of producing a cementitious composition disclosed herein, comprising a step of mixing the calcined clay

material with a carbonate material and a sulphate material, wherein the carbonate material is limestone, and wherein the sulphate material is gypsum.

In a preferred embodiment, the present disclosure accordingly provides for a method of producing a cementitious composition, comprising:

- 5 (a) heating a clay material at a maximum temperature of about 700 °C to about 900 °C to form a calcined clay material;
- (b) mixing the calcined clay material with a carbonate material selected from the group consisting of limestone, calcium magnesium carbonate, and mixtures thereof, and a sulphate material selected from the group consisting of gypsum, bassanite, anhydrite, and mixtures thereof to
- 10 form a supplementary cementitious mixture;
- (c) blending the supplementary cementitious mixture with Portland cement clinker,

wherein:

the Portland cement clinker is in an amount of from about 70 wt% to 95 wt% by dry weight based on the total dry weight of the cementitious composition;

- 15 the supplementary cementitious material in an amount from about 5 wt% to about 30 wt% by dry weight based on the total dry weight of the cementitious composition;

the weight ratio of the calcined clay material to the carbonate material is about 2:1.

Examples

- 20 Non-limiting examples of the invention and comparative examples will be further described in greater detail by reference to specific examples, which should not be construed as in any way limiting the scope of the invention.

Materials and Methods

- 25 Portland cement clinker (strength class 42.5 N, CEM I) was purchased from EnGro Corporation Limited.

Clay material (raw marine clay) was obtained from:

Place	Kaolinite (%)
Ulu Pandan, Singapore	29
Pulau Tekong, Singapore	29
Marina, Singapore	38
Changi, Singapore	33
Lorong Halus, Singapore	61

Unless otherwise indicated, the number behind LC³ and MC indicates the amount of substitution of OPC (i.e. LC³-10 means 10% of OPC was substituted with supplementary cementitious composition, LC³-20 means 20% of OPC was substituted with supplementary cementitious composition, etc.).

Example 1: Characterizing Starting Materials

The physical and chemical characterization of the marine clay (obtained from Changi, Singapore), Portland cement clinker and calcined clay material were conducted using a BET particle size analyzer, X-Ray Fluorescence (XRF), thermogravimetric analysis (TGA), X-ray diffraction (XRD) and magic angle spinning nuclear magnetic resonance (MAS NMR) techniques.

Table 1: Key Characteristics of Particle Size Analysis

Material	D ₁₀ (μm)	D ₅₀ (μm)	D ₉₀ (μm)	Specific surface area (m ² g ⁻¹)
Portland cement clinker	6.326	23.408	51.447	0.703
Clay material (Raw marine clay)	1.527	8.475	31.646	1.53

The particle size distribution of the Portland cement clinker and marine clay from the BET particle size analyzer are shown in **Figure 1**, with the key observations from this test reported in **Table 2**. The marine clay was found to have a D₅₀ of 8.475 μm, far smaller than that of the Portland cement clinker tested (23.408 μm). This shows that the marine clay is much finer than Portland cement clinker. Owing to its very fine size, a high surface area provides better reactivity. Furthermore, the unreacted calcined marine clay also advantageously acts as an efficient filler material.

Table 2: Chemical Composition of Marine Clay

Compounds	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	K ₂ O	CaO	MgO	Cl	Na ₂ O	SO ₃	TiO ₂	MnO	Total
Weight (%)	64.94	19.44	4.73	2.31	2.21	1.52	1.40	1.29	1.07	0.88	0.04	99.83

The chemical composition of marine clay was analyzed using the XRF technique and the major oxides observed are shown in **Table 2**. It is important to note that the SiO₂ and Al₂O₃ compounds combinedly form more than 80% of the clay material. However, the reactivity of these oxides depends on the mineral structure they are forming. Hence, it is essential to examine the major minerals present in raw clay material.

To accomplish that, the marine clay was further analyzed using XRD analysis to determine the major minerals present, with results indicating that quartz is the major constituent of marine clay (Figure 4). Illite and kaolinite minerals are also present but in significantly lower quantities than quartz.

The kaolinite content is an important factor in considering whether a clay may be used as a Supplementary Cementitious Material (SCM) or in Limestone Calcined Clay cement (LC³) binders. The kaolinite content is measured by conducting the thermogravimetric analysis (TGA) and Differential Thermal Analysis (DTA) of raw marine clay from room temperature to 900°C. The results obtained from TGA and DTA measurements are shown in Figure 2.

It is known that the dehydroxylation of kaolinite leads to the formation of metakaolin. The weight loss and DTA curves in Figure 2 show that kaolinite is dehydroxylated between 400°C to 560°C. The water loss during kaolinite dehydroxylation ($wt\%_{kaol-OH}$) allows the determination of the kaolinite content ($wt\%_{kaolinite}$) according to Eq. (1). $M_{kaolinite}$ and M_{water} refer to the molecular weights of kaolinite and water respectively.

$$wt\%_{kaolinite} = wt\%_{kaol-OH} \times \frac{M_{kaolinite}}{2M_{water}} \quad - (1)$$

By using Eq. (1) and the tangent method on Figure 2, the kaolinite concentration in marine clay is estimated to be about 29%.

Example 2: Activating Marine Clay

Kaolinite transforms into the reactive metakaolin form at about 500 – 900°C, which is the also reactive form of the mineral to participate in the hydration reactions of cement. Thus, thermal activation or calcination of marine clay is essential to utilize the kaolinite mineral present in it. The steps involved in

the transformation of raw marine clay to useable calcined marine clay is illustrated in Figure 3. Raw marine clay is first manually broken into small pieces, and then subsequently ground to powder form using a planetary ball miller for 5 minutes at 500 rpm. The powdered marine clay, after being passed through a 150 μ m sieve, is then calcined in the furnace. The powdered marine clay is heated at a rate of 10°C/min up to the peak temperature of 900 °C, after which the peak temperature is maintained for 2 hours to produce calcined marine clay. After holding, the calcined marine clay is allowed to gradually cool to room temperature and it is finally milled for 1 minute at 450 rpm to produce a working calcined marine clay to be used in subsequent experiments.

The appropriate calcination temperature of marine clay for maximum reactivity is determined by using different techniques and explained in the following section.

Example 3: Calcining Clay Material

The TGA study in Figure 2 shows that the dehydroxylation of kaolinite happens between 400 °C to 560 °C. However, the complete transformation of the kaolinite mineral to the amorphous metastable metakaolin phase takes place at a higher temperature than the dehydroxylation temperature. Consequently, it is necessary to determine the appropriate calcination temperature for the efficient conversion and use of the kaolinite present in marine clay.

In this regard, the microstructural changes resulting from different calcination temperatures ranging from 600 °C to 900 °C are studied using X-Ray Diffraction (XRD) analysis. Figure 4 shows the XRD pattern of marine clay at four different temperature, i.e., room temperature, 700 °C, 800 °C and 900 °C. While the main kaolinite peak reflected at 12.36° 2 θ in marine clay disappeared at 700 °C, the small initial kaolinite peak observed in the XRD spectra taken at room temperature suggests that the results from XRD may not be sufficient to determine the appropriate calcination temperature. A MAS-NMR analysis was therefore performed and it confirmed that at 700 °C, less reactive octahedral state of ²⁷Al nuclei exists, which completely transforms to more reactive tetrahedral state at 900 °C.

Figure 15 shows the zoomed-in XRD spectrum of the same marine clay but calcined at a temperature of 800 °C for 1 hour and 2 hours respectively. As observed, the peaks corresponding to kaolinite are not detected, but as above this is hardly indicative of a complete conversion of kaolinite to the active metakaolin form.

This result from XRD analysis was subsequently verified using the Magic-Angle Spinning Nuclear Magnetic Resonance (MAS-NMR) technique. All the experiments were run at ambient temperature in a Bruker 600 MHz NMR spectrometer equipped with a 4 mm probe. The samples were spun at the magic angle at 10 kHz and 14 kHz for ²⁹Si and ²⁷Al nuclei respectively. In this regard, the transformation of the

Si nuclei at different calcination temperatures, such as 600 °C, 700 °C, 800 °C, 850 °C and 900 °C are analysed and the corresponding spectra are shown in Figure 5 (for the ^{27}Al nuclei) and Figure 6 (for the ^{29}Si nuclei) respectively.

Earlier XRD analysis of the marine clay at room temperature (Figure 4) shows that the major aluminosilicate mineral present in marine clay is illite in addition to kaolinite. Kaolinite is a combination of 1:1 silica tetrahedra and aluminium octahedral sheets, whereas in illite the aluminium octahedral sheet is sandwiched between two silica tetrahedra sheets. Owing to such structural arrangements of kaolinite the OH groups attached to aluminium easily dehydroxylate during calcination in comparison to illite. Octahedral (Al^{VI}), pentahedral (Al^{V}) and tetrahedral (Al^{IV}) are three different coordination states of aluminium observed in kaolinite, whereas in illite Al^{VI} and Al^{IV} are usually detected. The unheated kaolinite mineral exhibits only Al^{VI} coordination state, whereas for illite mineral both Al^{VI} and Al^{IV} are observed. After complete dehydroxylation, Al^{V} and Al^{IV} coordination states are observed in kaolinite mineral, whereas only Al^{IV} coordination state is noticed in illite mineral. The peaks corresponding to the Al^{VI} and Al^{IV} coordination states for illite and kaolinite occur at 4.8 ppm and 71.5 ppm respectively.

Owing to the presence of both Al^{VI} and Al^{IV} coordination states in raw marine clay, it can be inferred that the illite mineral is dominant. Moreover, the peak corresponding to Al^{V} in kaolinite (around 20 ppm to 23 ppm) is absent after calcination at various temperatures, further indicating the significant presence of illite mineral in marine clay (Figure 5). The calcination of marine clay results in a gradual reduction in the intensity of Al^{VI} peak (4.8 ppm) and shifting of the centre of gravity (δ_{cg}) of Al^{IV} peak towards 60 ppm. It is noted that the Al^{VI} peaks are still observable at the earlier tested temperatures of 700 °C and 800 °C. However, at a calcination temperature of 900 °C the Al^{VI} peak is completely absent and only Al^{IV} peak is observed at δ_{cg} of 59 ppm.

The transformation in the ^{29}Si nuclei owing to calcination is shown in the MAS-NMR spectra in Figure 6. The sharp peak at -108 ppm corresponds to the presence of quartz. In addition to this a broad peak is also observed between -80 ppm to -100 ppm having a δ_{cg} about 92 ppm. This broad peak consists of overlapping of at least two resonances, i.e., Q^3 (0Al) and Q^3 (1Al) centered around -93 ppm and -88 ppm respectively. Upon calcination beyond 700 °C the δ_{cg} of the broad peak starts shifting towards a lower chemical frequency of about -94 ppm. This confirms the formation of amorphous aluminosilicate structure owing to the dehydroxylation process. The shifting of the δ_{cg} towards a lower frequency and broadening of the same peak can be further observed at 900 °C, which indicates a higher amorphization of the majority of the clay structure. Also, the distinguishable separation between the broad peak and quartz peak suggests that the recrystallization Q^3 -type silica to Q^4 -silica has not commenced at 900 °C. Accounting for the chemical transformations in ^{27}Al and ^{29}Si nuclei from NMR study, 900 °C can be suggested as the appropriate calcination temperature of marine clay.

Example 4: Gypsum Proportion

Prior to investing the replacement of Portland cement clinker with calcined clay material, the appropriate content of gypsum was first investigated. The gypsum content in the LC³ mixes was investigated using isothermal calorimetry. To that end, LC³-20 mixes with gypsum content of 4 wt%, 6 wt%, 8 wt%, and 10 wt% based on the total dry weight of LC³ (i.e. calcined marine clay, limestone and gypsum) were made (Table 3). Considering the duration at which a definite aluminate peak was formed in the heat evolution curve (Figure 10) and the cumulative heat evolution (Figure 11), the appropriate gypsum content was found to be 8 wt% (based on the total dry weigh of supplementary cementitious composition), This value was subsequently followed for all LC³ mixes and the resulting mix proportions are shown in Table 4. Although the LC³-20 mix with 10 wt% gypsum exhibits the highest cumulative heat evolution (Figure 11), the occurrence of aluminate peak is delayed to between 17 to 22 hours after the addition of water. In comparison, the aluminate peak in occurs at 15 to 20 hours after the addition of water (Figure 10). Hence, 8 wt% gypsum content (based on the total weight of LC³) is considered appropriate for the LC³ mixes.

Table 3: Mix Proportions of LC³-20 Mixes with Different Gypsum Content (100% OPC = 740 g)

Mix no.	Mixes	Cement (g)	Calcined marine clay (g)	Limestone (g)	Gypsum (g)	Wt% of gypsum based on total dry weight of LC ³	Sand (g)	Water (g)	Superplasticizer (g)
1	LC ³ -20	592	94.72	47.36	5.92	4 wt%	2035	359	-
2	LC ³ -20	592	93.24	45.88	8.88	6 wt%	2035	359	-
3	LC ³ -20	592	91.76	44.40	11.84	8 wt%	2035	359	-
4	LC ³ -20	592	88.80	44.40	14.80	10 wt%	2035	359	-

Example 5: Calcination temperature of LC³ Mixes

The appropriate calcination temperature was further confirmed via isothermal calorimetry of calcined at different temperatures, more specifically at 800 °C, 850 °C and 900 °C.

Figure 7 and Figure 8 show the heat evolution rate and cumulative heat evolution of LC³-20 mix (Mix no. 3 of Table 3) at different maximum temperatures. The LC³-20 mix prepared using clay material

calcined at 900 °C exhibits maximum cumulative heat evolution after 48 hours (Figure 8). The compressive strength of the MC-20 mix (Mix no. 8 of Table 4) calcined at different temperatures were also tested. To test that, the clay material was heated at a steady rate of 10 °C/min up to the different maximum temperatures i.e. 700 °C, 800 °C and 900 °C, and the maximum temperatures were maintained for 2 hours.

5 The calcined clay material was then allowed to cool down gradually to room temperature inside the furnace, and used subsequently in making the different MC-20 mixes. Results are shown in Figure 17. Figure 17 shows that the compressive strength of the mortar mixes was the highest when the clay material was calcined at 900 °C, further indicating that 900 °C is the appropriate maximum temperature for calcination.

10 Consequently based on the results here and in Example 4, the clay material is calcined at a maximum temperature of 900 °C in subsequent examples unless otherwise indicated.

Example 6: General Procedure for Preparing LC³ Mixes Using Calcined Clay Material

15 The Thermogravimetric Analysis study in Figure 2 showed that the marine clay used in this research contained about 29% by weight of kaolinite. In addition to this, the XRD studies (Figure 4) and NMR studies (Figures 5 and 6) confirm the presence of illite as the dominant aluminosilicate mineral. The NMR studies also confirm the complete activation of these minerals at 900 °C. The subsequent sections discuss the use of the calcined clay material as Supplementary Cementitious Material (SCM) as well as in LC³ binder.

20 In this regard, five replacement percentages of calcined clay material in the LC³ mixes, such as 10%, 20%, 30%, 40% and 50% by weight of the total LC³ mix were investigated. The ratio of the calcined clay material and limestone were kept at ~ 2:1 (2.067:1) in all cases. In MC mix, calcined clay material is used as a complete replacement for Portland cement clinker, whereas the LC³ mixes are prepared by replacing a portion of the Portland cement clinker with a mixture of calcined clay material, limestone and
25 gypsum. The detailed proportions of the various LC³ mixes are shown in Table 4. Superplasticizer were added to the MC-40 and MC-50 mixes due to their low workability.

The procedure for preparing the different cementitious compositions in Table 4, hereafter referred to as the LC³ mixes and MC mixes, is described below and summarized in Figure 9. In both LC³ and MC mixes, a dry mixture of sand and cementitious composition (cement+calcined marine
30 clay+limestone+gypsum in LC³ mixes and cement+calcined marine clay in MC mixes) was initially prepared. Superplasticizer was thoroughly mixed into water and the solution was gradually added to the dry mixture of sand and cementitious composition. The mixer was initially run at a slow speed (140 ± 5 r/min, r = revolutions) for 30 seconds, afterwhich it was run at a speed of 285 ± 10 r/min for another 30 seconds and stopped for 90 seconds. Subsequently, the mixing was finished by running the mixer for 60

seconds at a speed of 285 ± 10 r/min. This mixing procedure was performed following ASTM C305 – 20 (2020) standard.

Table 4: Mix Proportions of LC³ and MC Mixes

Mix No.	Mixes	Cement (g)	Calcined marine Clay material (g)	Limestone (g)	Gypsum (g)	Sand (g)	Water (g)	Superplasticizer (SP, % wt. of binder)
1	Control	740	-	-	-	2035	359	-
2	LC ³ -10	666	45.88	22.20	5.92	2035	359	-
3	LC ³ -20	592	91.76	44.40	11.84	2035	359	-
4	LC ³ -30	518	137.64	66.60	17.76	2035	359	-
5	LC ³ -40	444	183.52	88.80	23.68	2035	359	-
6	LC ³ -50	370	229.40	111.00	29.60	2035	359	-
7	MC-10	666	74	-	-	2035	359	-
8	MC-20	592	148	-	-	2035	359	-
9	MC-30	518	222	-	-	2035	359	-
10	MC-40	444	296	-	-	2035	359	0.7
11	MC-50	370	370	-	-	2035	359	0.8

Example 7: Calcined Clay Material Proportion

Table 5: Representative mixes

Mix	Water (g)	OPC (g)	Calcined marine clay (g)	Limestone (g)	Gypsum (g)
LC ³ (1 hr)	20	-	31	15	4
LC ³ (2 hrs)	20	-	31	15	4
LC ³ -30 (1 hr)	20	35	9.3	4.5	1.2
LC ³ -30 (2 hrs)	20	35	9.3	4.5	1.2

Figure 16a shows the cumulative heat evolution of various mixes with and without replacement of the Portland cement clinker with the cementitious composition of the present invention. It was observed that when the clinker was substituted with the cementitious composition, there was a significant increase in cumulative heat evolution in the first 48 hours after addition of water. In comparison, the unsubstituted mixes had negligible heat evolution.

Figure 16b shows the heat flow in the first 1 hour after addition of water. Results show that all the compositions had an initial increase in heat flow for the first 6 minutes, after which the heat flow decreased by the end of 1 hour. Figure 16c shows the heat flow in the first 48 hours after addition of water. As shown in Figure 16c, there was continuous heat flow in the first 48 hours after addition of water in the mixes where clinker was substituted with cementitious composition. In comparison, the unsubstituted mixes had negligible heat flow after the first hour, after addition of water.

Example 8: Compressive Strength of LC³

The preparation of mortar cubes is conducted in accordance to the guidelines suggested by ASTM C109/C109M-20b (2020). The prepared mortar mix was poured into 50 mm cube molds in two layers with each layer being 25 mm in height. Each layer was tamped with 32 strokes. After tamping the second layer, the excess mortar was removed and the surface was finished carefully with the help of a trowel. The specimens were removed from the molds after 24 h and placed in the water tank for curing.

The compressive strength of 50 mm mortar cubes as measured after 7 days and 28 days of curing. After the specimens were removed from the water tank, they were wiped with the help of dry cloth and left for about 1 – 2 h to achieve the surface-dry condition. The specimens were then placed at the center of the compressive testing machine and the load was applied in the orthogonal direction of placing of mortar. The specimens were tested at a rate of 60 kN/min. The compressive strength results are shown in Figure 12. Both LC³ and MC mixes exhibited lower compressive strength than the control mix (prepared using only OPC) after 7 days as well as 28 days of curing. Further it was observed that the compressive strength was reduced with an increasing amount of OPC replaced. After 28 days of curing the reduction in compressive strength is about 11.7% up to LC³-30 mix, whereas the reduction is about 20.9% up to MC-30 mix. A significant reduction in compressive strength results was further observed for mixes above a 30% replacement level of OPC. Up to 30% replacement of OPC, the compressive strength of LC³ mixes is always higher than MC mixes for both 7 days and 28 days. The compressive strength of LC³-30 is about 10.4% higher than MC-30 after 28 days of curing. Considering the available results, it can be concluded that the LC³ mixes are better than the MC mixes and up to 30% replacement of OPC with LC³ binder is ideal.

Example 9: Calcination Duration at Maximum Temperature on Compressive Strength

The effect of the calcination duration at the maximum temperature on compressive strength was investigated on LC³-30 in Table 4 (Mix no. 4), with results as shown in Figure 14. An increase in compressive strength was observed in both cases (7 days and 28 days of curing) when the duration at which the maximum temperature was held during the calcination increased from 1 hour to 2 hours. Accordingly, an increase of 7.6% was observed for the mortar cured for 7 days, while an increase of 2.4% was observed for the mortar cured for 28 days. Results show that a longer holding duration during calcination conversely results in mortar with higher compressive strength. Accordingly, it also suggests that a shorter curing duration may be needed when calcination is held for longer.

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Example 10: Thermal properties of LC³**Table 6**

Binder/sand mass ratio	0.36
Water/binder mass ratio	0.4
Curing time (day)	7, 14, 28, 56
Curing conditions	Air and water
OPC:calcined marine clay:limestone:gypsum (LC ³ -30)	0.7:0.186:0.09:0.024

From Figure 13a, all samples (OPC and LC³-30 from Table 4) exhibited decreasing thermal conductivities as the curing duration was increased from 7 days to 56 days both in air and in water. The process for curing in water is briefly described. Normal tap water was added into a water tank, after which the samples were immersed completely inside the water tank. The samples were left inside the water tank at ambient conditions with no temperature adjustments made and were allowed to cure up until the desired curing duration was reached. The results from Figure 13a further reveal that the thermal conductivity of the samples were increased across all curing conditions in air when 30% of the OPC was replaced with calcined clay material. Conversely, the thermal conductivities of the samples were reduced across all curing conditions in water when 30% of the OPC was replaced with calcined clay material. It is ultimately noted that the thermal conductivity of the LC³-30 samples are comparable to those of the OPC mixes, and that a good portion of the OPC may be replaced without affecting the thermal properties of the cementitious compositions.

The thermal diffusivities and volumetric heat capacities of the cementitious compositions when OPC was replaced by calcined clay material are further shown in Figure 13b and Figure 13c respectively. As observed earlier from Figure 13a, the samples when OPC is replaced by calcined clay material exhibited comparable thermal properties (under various curing duration and conditions). These results further show that the thermal properties are not significantly affected when calcined clay material was used as replacement for OPC, validating the use of the marine clay disclosed in the present disclosure in cementitious compositions.

Industrial Applicability

The present disclosure focuses on using marine clay as a replacement for Portland cement clinker and in doing so provide a new use for such waste material. Further, the replacement of Portland cement clinker with calcined clay material also results in a smaller carbon footprint, as the calcination temperature for the clay material is much lower as compared to that of the cement clinker. Thus the present invention also results in energy savings as well as lower fuel used in comparison to conventional cement. The cementitious composition of the present invention also involves non-hazardous materials, such as calcined marine clay, limestone and gypsum. Moreover, the simple processing and application procedure requires limited expertise, which encourages its large-scale application as a partial replacement of Portland cement clinker.

It will be apparent that various other modifications and adaptations of the invention will be apparent to the person skilled in the art after reading the foregoing disclosure without departing from the spirit and scope of the invention and it is intended that all such modifications and adaptations come within the scope of the appended claims.

Claims

1. A cementitious composition comprising:
 - (a) Portland cement clinker in an amount of from about 70 wt% to about 95 wt% by dry weight based on the total dry weight of the cementitious composition; and
 - (b) supplementary cementitious material in an amount from about 5 wt% to about 30 wt% by dry weight based on the total dry weight of the cementitious composition, wherein the supplementary cementitious material comprises:
 - (i) calcined clay material produced from heating a clay material at a maximum temperature of between about 700 °C to about 900 °C;
 - (ii) carbonate material selected from the group consisting of limestone, calcium magnesium carbonate, and mixtures thereof; and
 - (iii) sulphate material selected from the group consisting of gypsum, bassanite, anhydrite, and mixtures thereof,wherein the weight ratio of the calcined clay material to the carbonate material is about 1.5:1 to about 2.1:1 .
2. The cementitious composition of claim 1, wherein the clay material contains at least about 25 wt% kaolinite.
3. The cementitious composition of claim 1 or 2, wherein the clay material contains at least about 25 wt% to about 35 wt% kaolinite.
4. The cementitious composition of any one of claims 1 to 3, wherein the calcined clay material is produced by heating the clay material at a maximum temperature of about 900 °C.
5. The cementitious composition of any one of claims 1 to 4, wherein the calcined clay material is produced from heating the clay material at a rate of about 5 °C to about 15 °C per minute up to the maximum temperature, and the maximum temperature is maintained for at least 1 hour.
6. The cementitious composition of any one of claims 1 to 5, wherein the calcined clay material is produced from heating the clay material at a rate of about 10 °C per minute up to the maximum temperature, and the maximum temperature is maintained for at least 1 hour.
7. The cementitious composition of any one of claims 1 to 6, wherein the maximum temperature is maintained for at least 2 hours.

8. The cementitious composition of any one of claims 1 to 7, wherein the weight ratio of the calcined clay material to the carbonate material is about 2:1 to about 2.1:1.
- 5 9. The cementitious composition of any one of claims 1 to 8, wherein the weight ratio of the calcined clay material to the carbonate material is about 2.067:1.
- 10 10. The cementitious composition of any one of claims 1 to 9, wherein the weight ratio of the calcined clay material to the sulphate material is about 7:1 to about 8:1.
- 11 11. The cementitious composition of any one of claims 1 to 10, wherein the weight ratio of the calcined clay material to the sulphate material is about 7.75:1.
- 15 12. The cementitious composition of any one of claims 1 to 11, wherein the sulphate material is present in the range of 1 wt% to about 10 wt% by dry weight based on the total dry weight of supplementary cementitious material.
- 20 13. The cementitious composition of any one of claims 1 to 12, wherein the supplementary cementitious material in an amount from about 5 wt% to about 30 wt% by dry weight based on the total dry weight of the cementitious composition.
14. The cementitious composition of any one of claims 1 to 13, wherein the carbonate material is limestone.
- 25 15. The cementitious composition of any one of claims 1 to 14, wherein the sulphate material is gypsum.
16. A cementitious composition, comprising:
- 30 (a) Portland cement clinker in an amount of from about 70 wt% to 80 wt% by dry weight based on the total dry weight of the cementitious composition; and
- (b) supplementary cementitious material in an amount from about 20 wt% to about 30 wt% by dry weight based on the total dry weight of the cementitious composition,
- wherein the supplementary cementitious material comprises:
- 35 (i) calcined clay material produced from heating a clay material at a maximum temperature of about 700 °C to about 900 °C, wherein the clay material contains at least about 25 wt% to about 35 wt% kaolinite;
- (ii) limestone; and

(iii) gypsum,

wherein the weight ratio of the calcined clay material to the limestone is about 2:1 to about 2.1:1 .

17. A method of producing a cementitious composition, comprising:

- 5 (a) heating a clay material at a maximum temperature of about 700 °C to about 900 °C to form a calcined clay material;
- (b) mixing the calcined clay material with a carbonate material selected from the group consisting of limestone, calcium magnesium carbonate, and mixtures thereof, and a sulphate material selected from the group consisting of gypsum, bassanite, anhydrite, and mixtures thereof to
- 10 form a supplementary cementitious mixture;
- (c) blending the supplementary cementitious mixture with Portland cement clinker,

wherein:

the Portland cement clinker is in an amount of from about 70 wt% to 95 wt% by dry weight based on the total dry weight of the cementitious composition;

- 15 the supplementary cementitious material in an amount from about 5 wt% to about 30 wt% by dry weight based on the total dry weight of the cementitious composition;

the weight ratio of the calcined clay material to the carbonate material is about 1.5:1 to about 2.1:1.

18. The method of claim 17, wherein step (a) is performed at a maximum temperature of about 700
- 20 °C to about 900 °C, wherein the clay material is heated at a rate of about 5 °C to about 15 °C per minute up to the maximum temperature, and the maximum temperature is maintained for at least 1 hour.

19. The method of claim 17 or 18, wherein step (a) is performed at a maximum temperature of about
- 25 700 °C to about 900 °C, wherein the clay material is heated at a rate of about 10 °C per minute up to the maximum temperature, and the maximum temperature is maintained for at least 1 hour.

20. The method of any one of claims 17 to 19, wherein step (a) is performed at a maximum
- temperature of about 700 °C to about 900 °C, wherein the clay material is heated at a rate of
- 30 about 10 °C per minute up to the maximum temperature, and the maximum temperature is maintained for at least 2 hours.