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Patent application No.

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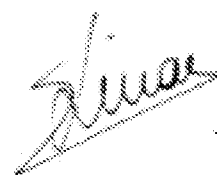
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Method of producing a pozzolanic material for use in a low-carbon element

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The invention refers to a method of producing a pozzolanic material for use in a low-carbon cement. Further, the invention refers to a hydraulic cement comprising Portland cement, an additional material and a pozzolanic material.

5

Cement production is one of the most significant sources of anthropogenic carbon dioxide (CO₂) emissions, accounting for approximately 7-8% of global CO₂ emissions. This is primarily due to the fact that the production of traditional Portland cement involves the calcination of limestone (calcium carbonate), a process that releases a significant amount of CO₂. Furthermore, the energy-intensive nature of cement production, which often involves burning fossil fuels, contributes additional CO₂ emissions.

15

Low-carbon cements, also known as green or sustainable cements, have been developed to address these environmental concerns. These types of cements aim to significantly reduce the carbon footprint associated with cement production. This is achieved by altering the composition and manufacturing process of the cement, in order to decrease the amount of CO₂ produced per unit of cement produced.

25

One of the main ways in which low-carbon cements achieve this reduction is by replacing some of the clinker with other materials. Examples of such substitutions include the use of industrial byproducts such as fly ash and slag, as well as naturally occurring materials like pozzolana, or calcined clays. An example of a low-carbon cement is the Limestone Calcined Clay Cement (LC3), a composite binder comprising clinker, calcined clay, limestone, and gypsum.

30

However, the practical implementation of low-carbon cement production based on calcined clay presents several challenges. Foremost among these is the requirement for the raw clay used to produce the calcined clay component of the cement to have a high content of kaolinite, typically no less than 40%. Unfortunately, it is not uncommon to encounter clay materials with kaolinite contents below this threshold, typically not exceeding 25%. This low percentage makes them unsuitable for the production of low-carbon cement under conventional conditions.

Kaolinite has a layered silicate structure, composed of alternating layers of tetrahedral sheets of silica and octahedral sheets of alumina linked with each other by oxygen atoms. When kaolinite is heated during the calcination process, a sequence of reactions occurs leading to the dehydroxylation (loss of water) and transformation of the kaolinite into an amorphous material known as metakaolin.

Metakaolin is highly reactive in a cementitious environment. It reacts with calcium hydroxide (produced during the hydration of Portland cement) in a process known as pozzolanic reaction, forming calcium silicate hydrates (C-S-H), calcium aluminate hydrates and calcium aluminate silicate hydrates. All these products contribute significantly to the compressive strength of the cement. They are the main binders in concrete and responsible for the strength development. The greater the volume of binders produced, the higher the compressive strength of the resulting cementitious matrix. Therefore, a higher kaolinite content, which leads to more metakaolin, allows for more binder formation and results in higher compressive strength.

Thus, the requirement for high kaolinite content in the clay used for low-carbon cement production is tied directly to the contribution of the resulting metakaolin to the mechanical performance of the cement, particularly its compressive strength. Using clay with a lower kaolinite content without compensating for the decrease in reactivity could lead to a drop in the cement's mechanical performance.

One potential solution to this problem was proposed in FR 3084665 B1. The patent suggests the use of clay with a kaolinite content of less than 25%, but with a significant amount of muscovite and/or illite, constituting at least 20%, to make a cementitious material. However, when the cementitious material produced in this manner is used in a cement formulation where the Portland cement (CEM I) component is less than 70%, the mechanical performance of the resulting composite cement suffers a significant decrease. This substantial drop in performance prevents the production of a low-clinker or low-CEM I cement with acceptable performance characteristics using such clay materials.

Therefore, the instant invention aims at enabling the production of a low-carbon cement using clay with low kaolinite content without compromising compressive strength performance.

To solve this object, the invention provides a method of producing a pozzolanic material for use in a low-carbon cement, comprising

- providing an argillaceous material that comprises 1 - 49 wt.-% kaolinite, 1 - 49 wt.-% muscovite and < 5 wt.-% calcite,

- mixing the argillaceous material with a source of calcium oxide,
- co-calcining the argillaceous material and the source of calcium oxide at a temperature of 700-900°C over a time period of 15-240 min, thereby obtaining the pozzolanic material.

The invention is based on the surprising finding that the co-calcination of a clay material having a low kaolinite content with a source of calcium oxide provides a pozzolanic material that, when used as a cementitious material in a low-carbon cement, compensates for the loss of compressive strength that would otherwise occur due to the low kaolinite content.

- 15 The combination of muscovite with a source of calcium oxide, when being co-calcined, appears to have a synergistic effect contributing to the compressive strength of the resulting cementitious material leading to improved compressive strength values despite low kaolinite content. This ensures that even clays with low kaolinite content can be effectively used in the production of low-carbon cement.

Preferably, limestone may be used as the source of calcium oxide. However, alternative sources of calcium oxide may also be used. Preferably, at least one member selected from the group consisting of steel slag, blast furnace slag, CaO rich fly ash, free lime, paper sludges, and recycled concrete fines, may be used as the source of calcium oxide. As used herein, a source of calcium oxide is considered to refer to any mineral material that contains calcium oxide or that contains a mineral phase that, upon calcination at a temperature of 700-900°C, is at least partially transformed into calcium oxide (CaO).

Preferably, the material that is used as the source of calcium oxide contains > 10 wt.-%, preferably > 20 wt.-%, of calcite, or > 5 wt.-%, preferably > 10 wt.-% of calcium oxide. In case the source of calcium oxide contains both calcite and calcium oxide, the sum of both preferably is at least 10 wt.-% of said material. Preferably, the material that is used as the source of calcium oxide contains < 15 wt.-% MgO.

10

The argillaceous material that is co-calcined with the source of calcium oxide may also contain calcite or calcium oxide. In this case a minimum amount of calcium oxide and/or calcite may preferably be defined based on the combined content of calcium oxide and/or calcite in the argillaceous material and the source of calcium oxide.

15

Preferably, the mixture of argillaceous material and the source of calcium oxide contains > 10 wt.-%, preferably 20 wt.-%, calcite. Preferably, the upper limit for the calcite content is 25 wt.-% or 20 wt.-%. Exceeding a content of 25 wt.-% or 20 wt.-% of calcite, as the case may be, could result in an excessive dilution of the reactive clay components in the mixture.

25

Preferably, the mixture of argillaceous material and the source of calcium oxide contains > 5 wt.-%, preferably 10 wt.-%, calcium oxide. Preferably, the upper limit for the calcium oxide content is 12.5 wt.-% or 25.5 wt.-%. Exceeding a content of 12.5 wt.-% or 25.5 wt.-% of calcium oxide, as the case may be, could result in an excessive dilution of the reactive clay components in the mixture.

30

According to the invention, the argillaceous material comprises 1 - 49 wt.-% kaolinite. Preferably, the argillaceous material may contain < 45 wt.-%, < 40 wt.-%, < 35 wt.-%, < 30 wt.-%, < 25 wt.-%, < 20 wt.-%, < 15 wt.-% or
5 < 10 wt.-% kaolinite. In any case, the minimum content of kaolinite in the argillaceous material preferably is 1 wt.-%, more preferably 5 wt.-%.

Preferably, the argillaceous material comprises 1-40 wt.-%
10 kaolinite, and even more preferably, the argillaceous material comprises 1-30 wt.-% kaolinite.

According to the invention the argillaceous material contains 1-49 wt.-% muscovite. Preferably, the argillaceous material
15 contains > 1 wt.-%, preferably > 10 wt.-% or > 20 wt.-% or > 30 wt.-% muscovite.

Preferably, the argillaceous material contains 10-74 wt.-% illite and/or smectite. This is understood to refer to the
20 combined content of illite and smectite if both minerals are present, or to the content of illite or smectite only, if the respective other mineral is absent.

Preferably, the argillaceous material contains 20-35 wt.-%,
25 illite and/or smectite. Other preferred ranges are characterized by a lower limit of 10, 15, 20 or 25 wt.-% and by an upper limit of 30, 40, 50 or 74 wt.-%, wherein any combination of any one of the lower limits and any one of the upper limits is disclosed herewith.

30 Preferably, the combined content of illite and smectite in the argillaceous material is < 50 wt.-%, preferably < 40 wt.-%, most preferably < 30 wt.-%.

- Any content of kaolinite, illite, muscovite, and calcite or any other mineral phase indicated in wt.-% is measured by XRD Rietveld method. X-ray diffraction (XRD) measurements were
- 5 made of powdered samples which were hand ground to pass a 63 μm sieve. A D8 Advance X-ray Diffractometer from Bruker was used which was operated using Cu K α radiation at an acceleration voltage of 25 kV and a current of 40 mA, scanning at 2 θ range of 3-65°, with 4336 steps and a counting
- 10 time of 0.135 s per step, rotation of the sample. The quantification of the phases present in the samples was achieved by Rietveld refinement using Topas Academic v6 software.
- 15 The calcium oxide content is measured by X-ray Fluorescence (XRF).

- According to the invention, co-calcining the argillaceous material and the source of calcium oxide is performed at a
- 20 temperature of 700-900°C in order to obtain a pozzolanic material. Co-calcination at said temperature is carried out in order to have the kaolinite component of the argillaceous material at least partially transform to metakaolin. Preferably, the co-calcination step is carried out so that at
- 25 least 70 wt.-% of the kaolinite has completely transformed into metakaolin. In the present invention, the co-calcination of the argillaceous material and the source of calcium oxide must not be done at a temperature above 900°C as this would like to the production of a dead-burnt material that has less
- 30 pozzolanic reactivity. Preferably, the co-calcination step is carried out at a temperature of 700-900°C over a time period of 15-240 minutes, preferably at a temperature of 700-900°C

over a time period of 15-180 minutes, even more preferably at a temperature of 700-900°C over a time period of 60-180 min.

Several prior art methods may be used for calcining the mixture of the argillaceous material and the source of calcium oxide, with the choice of the method being determined by factors such as the scale of production, the specific nature of the raw materials, and the desired characteristics of the final product.

According to one alternative a rotary kiln calcination is carried out. This involves feeding the mixture of argillaceous material and the source of calcium oxide into a rotating cylindrical furnace, where it is heated to the desired temperature range of 700-900°C. The rotation of the kiln ensures thorough mixing and even heating of the material, promoting consistent and efficient decarbonation of the calcium oxide source, such as limestone, and dehydroxylation of the clay minerals.

Alternatively, a vertical shaft kiln may be used for calcination. The mixture is loaded at the top of a tall, vertical furnace and heated as it descends through the kiln, undergoing the necessary chemical transformations.

Alternatively, a fluidized bed calcination may be used, which is a method wherein the mixture is suspended in a rising flow of hot gas. This ensures very high heat and mass transfer rates, providing rapid, uniform calcination.

Any type of argillaceous material may be used that contains the amounts of kaolinite, illite and muscovite indicated above. The argillaceous material may for example be a clay

material or a shale material. The main components of shale are clay minerals, quartz and calcite.

The argillaceous material may comprise any of the following
5 mineral components, in addition to kaolinite and illite and/or muscovite: quartz (up to 49 wt.-%), dolomite, albite, chlorite, microcline and calcite.

According to a preferred embodiment of the invention, the
10 argillaceous material, before being subjected to the step of co-calcining, is ground to a particle size characterized by a $D_{90} < 200\mu\text{m}$, preferably $< 100\mu\text{m}$. This enhanced surface area facilitates more efficient heat transfer and chemical
interactions during the co-calcination process, leading to
15 more effective dehydroxylation of clay minerals and decarbonation of the calcium source.

The D_{90} corresponds to the 90th centile of the volume distribution of particle sizes, i.e. 90% of the volume
20 consists of particles for which the size is less than the measured value. The D_{90} of particles is generally determined by laser diffraction. The particle size distribution of the different powders are obtained with a laser Malvern MS2000 granulometer. The measurement is carried out in a suitable
25 medium (for example, in an aqueous medium); the size of the particles should be comprised between $0.02\mu\text{m}$ and 2mm . The light source consists of a red He-Ne laser (632nm) and a blue diode (466nm). The optical model is the Fraunhofer one, the computation matrix is of the polydisperse type.

30

A measurement of background noise is first of all carried out with a pump rate of 2,000 rpm, a stirring rate of 800 rpm and a measurement of noise over 10 s, in the absence of

ultrasonic waves. It is then checked that the light intensity of the laser is at least equal to 80%, and that a decreasing exponential curve is obtained for the background noise. If this is not the case, the lenses of the cell have to be
5 cleaned. A first measurement is then carried out on the sample with the following parameters: pump rate of 2,000 rpm, stirring rate of 800 rpm, absence of ultrasonic waves, obscuration limit between 10 and 20%. The sample is introduced in order to have an obscuration slightly greater
10 than 10%. After stabilization of the obscuration, the measurement is carried out with a duration between the immersion and the measurement set to 10 s. The measurement duration is of 30 s (30,000 analyzed diffraction images). In the obtained granulogram, the fact that a portion of the
15 population of the powder may be agglomerated should be taken into account.

Next, a second measurement (without emptying the tank) is carried out with ultrasonic waves. The pump rate is brought
20 to 2,500 rpm, the stirring to 1,000 rpm, the ultrasonic waves are 100 % emitted (30 Watts). This rate is maintained for 3 minutes, and then one returns to the initial parameters: pump rate 2,000 rpm, stirrer rate of 800 rpm, absence of ultrasonic waves. After 10 s (for removing the possible air
25 bubbles), a measurement is made for 30 s (30,000 analyzed images). This second measurement corresponds to a powder de-agglomerated by ultrasonic dispersion. Each measurement is repeated least twice in order to check the stability of the result. The apparatus is calibrated before each working
30 session by means of a standard sample (silica C10 Sifraco) the grain size curve of which is known. All the measurements shown in the description and the announced ranges correspond to the values obtained with ultrasonic waves.

Particle size reduction also ensures the uniformity of the mixture with the calcium oxide source. This homogeneity fosters even heating and consistent chemical reactions during co-calcination, which translates into a more predictable and controlled quality of the final product. The small particle size also enables better incorporation of the calcined product within the cement matrix, thus enhancing the mechanical properties of the resulting cement, such as strength and durability.

According to another preferred embodiment, the argillaceous material may be dried before being subjected to the grinding step. Drying may be performed at a temperature of 90-120, preferably 100-110°C.

The step of mixing the argillaceous material with the source of calcium oxide may be performed in any suitable mixing device. Preferably, the mixing step may be conducted in a grinding device, such as in a ball mill. The mixture of the argillaceous material and the source of calcium oxide may be ground to a fineness characterised by a $D_{90} < 200 \mu\text{m}$, preferably $D_{90} < 100 \mu\text{m}$. By reducing the particle size, the total surface area of the material available for reactions during co-calcination significantly increases. This enhanced surface area facilitates more efficient heat transfer and chemical interactions during the co-calcination process, leading to more effective dehydroxylation of clay minerals and decarbonation of the calcium source.

30

The ratio of the argillaceous material and the source of calcium oxide preferably is in the range of 95/5 - 70/30 (w/w), preferably 90/10 - 75/25 (w/w).

According to a preferred embodiment, the ratio of the argillaceous material and the source of calcium oxide is selected so that the mixture of argillaceous material and the source of calcium oxide contains > 5 wt.-%, preferably 10-25 wt.-% or 10-20 wt.-%, calcium oxide.

According to a second aspect, the invention provides a hydraulic cement, comprising 45-70 wt.-% Portland cement, an additional material selected from the group consisting of ground granulated blast-furnace slag, silica fume, natural pozzolana, siliceous fly ash, calcareous fly ash, burnt shale and limestone, and a pozzolanic material obtained by a method according to the first aspect of the invention. Hence, a low-carbon cement is provided that has a reduced clinker content and that, due to the presence of the pozzolanic material of the invention, still has an acceptable compressive strength. In particular, the hydraulic cement of the invention has an improved compressive strength when compared to a reference cement that comprises the same amount of calcined aluminosilicate material, but without the addition of a source of calcium oxide.

Preferably, the hydraulic cement may comprise 45-60 wt.-%, preferably 45-50 wt.-%, Portland cement. The term "Portland cement", also referred to as "Ordinary Portland Cement (OPC)", refers to a type of hydraulic cement that sets, hardens, and adheres to other materials to bind them together. The primary components of Portland cement are calcium, silicon, aluminum, and iron, which are typically derived from limestone, clay, and other natural materials. These materials are crushed, combined, and heated in a kiln to a high temperature to produce clinker. This clinker is

then ground into a fine powder, often with a small amount of gypsum added to control the setting time of the final product.

5 Therefore, the Portland cement preferably is a cement of the type "CEM I", as defined in European standard EN 197-1:2011. It consists of 95-100% Portland cement clinker and up to 5% of a minor additional constituent, such as limestone or gypsum, that enhances the properties or the workability of
10 the cement.

Preferably, the hydraulic cement of the invention is a cement of the type CEM II/C-M, as defined in European standard NF EN 197-5:2021. This type of cement is defined by a Portland
15 cement content of 50-64 wt.-%, a combined content of the additional material and the pozzolanic material of 36-50 wt.-% and an optional content of minor additional constituents (0-5 wt.-%).

20 According to a preferred embodiment of the invention, the additional material is limestone.

Preferably, the hydraulic cement of the invention is a cement of the type CEM II/C-M (Q-LL), as defined in European
25 standard EN 197-5:2021. This type of cement is defined by a Portland cement content of 50-64 wt.-% and a combined content of limestone and the pozzolanic material of 36-50 wt.-%.

Preferably, the hydraulic cement of the invention comprises
30 15-30 wt.-% of the additional material, in particular limestone.

Preferably, the hydraulic cement of the invention comprises 15-30 wt.-% of the pozzolanic material.

Preferably, the combined amount of the additional material and the pozzolanic material is < 50 wt.-%, preferably 30-50 wt.-%.

As used herein, any content of Portland cement, the additional material and the pozzolanic material given in wt.-% is based on the total weight of the hydraulic cement.

In the following, the invention will be described in more detail with reference to the following examples.

Four different sources of argillaceous material were used as a raw material for preparing a pozzolanic material. Table 1 indicates the mineral composition of the raw materials according to Examples 1-4. All values are given in wt.-%. The mineralogical composition of the materials was measured by the XRD Rietveld method. The Rwp (weighted profile R value) given in the last line of Table 1 is the value that indicates how good or bad the predicted fitting is as compared to the experimental setting. The lower this value the better the prediction.

Table 1:

	Ex.1	Ex.2	Ex.3	Ex.4
	Raw clay 1	Raw clay 2	Raw clay 3	Raw clay 4
Montmorillonite	0	0	0	0,4
Muscovite 2M1	18	20	21	0,3
Muscovite 2M2	4	3,5	3,2	0,3
Chlorite lib	4	4,6	2,2	1,4
Clinocllore-1Mlib	0	0,0	0,0	0,0
Kaolinite	18	18,5	5,9	47,9
Quartz	33	19,3	38,6	42,1
Albite	2	3,4	0,6	0,2

Andesine An50	0	0,0	0,0	0,0
Anorthite	0	0,0	0,0	0,0
Microcline	3	4,2	9,3	0,7
Hematite	1	0,5	0,4	2,6
Goethite	0	0,0	0,0	0,0
Gibbsite	0	0,0	0,0	0,0
Bayerite	0	0,0	0,0	0,0
Anatase	0	0,1	0,1	0,5
Calcite	0	2,7	0,2	0,0
Dolomite	0	7,3	8,9	0,0
Pyrite	0	0,0	1,2	0,2
Alunite	1	0,6	0,3	0,8
Actinolite	0	0,0	0,0	0,0
Illite modified	7	7,1	4,5	2,1
Illite-smectite	8	6,6	2,9	0,0
Siderite	0	0,5	0,2	0,3
Oligoclase An25	1	1,2	0,0	0,0
Sanidine Na0.56	1	0,2	0,6	0,3
Rwp	8	7	8	10

In all examples, the argillaceous raw material was dried at 105°C and then ground until a particle diameter $d_{90} < 200 \mu\text{m}$. Subsequently, the argillaceous raw material was mixed with limestone, i.e. the product "BL200" supplied by Omya, consisting of 100 wt.-% calcite (CaCO_3). Mixing was carried out in a planetary ball mill PM 400 from Retsch for less than 10 minutes.

10 Example 1

The raw clay 1 of Example 1 and limestone were used in different mixing ratios. In Example 1.1, the raw clay 1 was used without any limestone being added as a reference example. In Examples 1.2, 1.3 and 1.4 the raw clay 1 was mixed with limestone in a ratio of 90/10, 80/20 and 60/40, respectively. The mineralogical composition of Examples 1.1, 1.2, 1.3 and 1.4 is given in Table 2. All values are given in wt.-%.

20 Table 2:

	Ex. 1.1	Ex. 1.2	Ex. 1.3	Ex. 1.4
	Raw clay 1	Raw clay 1 + BL200 (90/10)	Raw clay 1 + BL200 (80/20)	Raw clay 1 + BL200 (60/40)
Montmorillonite	0,0	0,0	0,0	0,0
Muscovite 2M1	18,4	16,1	14,3	10,7
Muscovite 2M2	4,1	3,9	3,5	2,6
Chlorite lib	3,9	3,9	3,5	2,6
Clinochlore-1Mlib	0,0	0,0	0,0	0,0
Kaolinite	18,0	16,5	14,6	11,0
Quartz	32,8	29,1	25,8	19,4
Albite	1,8	1,8	1,6	1,2
Andesine An50	0,0	0,0	0,0	0,0
Anorthite	0,0	0,0	0,0	0,0
Microcline	2,6	2,0	1,7	1,3
Hematite	0,6	0,5	0,4	0,3
Goethite	0,0	0,0	0,0	0,0
Gibbsite	0,0	0,0	0,0	0,0
Bayerite	0,0	0,0	0,0	0,0
Anatase	0,0	0,0	0,0	0,0
Calcite	0,1	10,0	19,9	39,8
Dolomite	0,2	0,0	0,0	0,0
Pyrite	0,3	0,0	0,0	0,0
Alunite	0,7	0,6	0,6	0,4
Actinolite	0,0	0,0	0,0	0,0
Illite modified	6,9	6,2	5,5	4,2
Illite-smectite	7,6	7,3	6,5	4,9
Siderite	0,3	0,0	0,0	0,0
Oligoclase An25	0,9	0,8	0,7	0,5
Sanidine Na0.56	0,6	0,5	0,5	0,3

Example 2

In Example 2.1, the raw clay 2 was used without any limestone being added as a reference example. In Examples 2.2, 2.3 and 2.4 the raw clay 2 was mixed with limestone in a ratio of 90/10, 80/20 and 60/40, respectively. The mineralogical composition of Examples 2.1, 2.2, 2.3 and 2.4 is given in Table 3. All values are given in wt.-%.

Table 3:

	Ex. 2.1	Ex. 2.2	Ex. 2.3	Ex. 2.4
	Raw clay 2	Raw clay 2 + BL200 (90/10)	Raw clay 2 + BL200 (80/20)	Raw clay 2 + BL200 (60/40)

Montmorillonite	0,0	0,0	0,0	0,0
Muscovite 2M1	19,8	19,6	17,4	13,1
Muscovite 2M2	3,5	2,5	2,2	1,7
Chlorite lib	4,6	4,7	4,2	3,1
Clinocllore-1Mlib	0,0	0,0	0,0	0,0
Kaolinite	18,5	15,6	13,9	10,4
Quartz	19,3	17,8	15,8	11,9
Albite	3,4	3,6	3,2	2,4
Andesine An50	0,0	0,0	0,0	0,0
Anorthite	0,0	0,0	0,0	0,0
Microcline	4,2	3,8	3,4	2,5
Hematite	0,5	0,5	0,4	0,3
Goethite	0,0	0,0	0,0	0,0
Gibbsite	0,0	0,0	0,0	0,0
Bayerite	0,0	0,0	0,0	0,0
Anatase	0,1	0,3	0,3	0,2
Calcite	2,7	11,9	21,7	41,1
Dolomite	7,3	5,9	5,3	3,9
Pyrite	0,0	0,0	0,0	0,0
Alunite	0,6	0,4	0,4	0,0
Actinolite	0,0	0,0	0,0	0,0
Illite modified	7,1	6,1	5,4	4,1
Illite-smectite	6,6	5,7	5,1	3,8
Siderite	0,5	0,4	0,3	0,3
Oligoclase An25	1,2	1,1	1,0	0,7
Sanidine Na0.56	0,2	0,0	0,0	0,0

Example 3

In Example 3.1, the raw clay 3 was used without any limestone being added as a reference example. In Examples 3.2, 3.3 and 3.4 the raw clay 3 was mixed with limestone in a ratio of 90/10, 80/20 and 60/40, respectively. The mineralogical composition of Examples 3.1, 3.2, 3.3 and 3.4 is given in Table 4. All values are given in wt.-%.

Table 4:

	Ex. 3.1	Ex. 3.2	Ex. 3.3	Ex. 3.4
	Raw clay 3	Raw clay 3 + BL200 (90/10)	Raw clay 3 + BL200 (80/20)	Raw clay 3 + BL200 (60/40)
Montmorillonite	0,0	0,0	0,0	0,0
Muscovite 2M1	21,0	18,9	16,8	12,6
Muscovite 2M2	3,2	2,8	2,5	1,9

Chlorite lib	2,2	2,0	1,8	1,3
Clinochlore-1MIIb	0,0	0,0	0,0	0,0
Kaolinite	5,9	5,3	4,7	3,6
Quartz	38,6	34,7	30,9	23,1
Albite	0,6	0,5	0,5	0,3
Andesine An50	0,0	0,0	0,0	0,0
Anorthite	0,0	0,0	0,0	0,0
Microcline	9,3	8,4	7,5	5,6
Hematite	0,4	0,3	0,3	0,2
Goethite	0,0	0,0	0,0	0,0
Gibbsite	0,0	0,0	0,0	0,0
Bayerite	0,0	0,0	0,0	0,0
Anatase	0,1	0,1	0,1	0,1
Calcite	0,2	10,1	20,1	39,9
Dolomite	8,9	8,0	7,1	5,3
Pyrite	1,2	1,1	1,0	0,7
Alunite	0,3	0,3	0,3	0,2
Actinolite	0,0	0,0	0,0	0,0
Illite modified	4,5	4,1	3,6	2,7
Illite-smectite	2,9	2,6	2,3	1,7
Siderite	0,2	0,2	0,1	0,1
Oligoclase An25	0,0	0,0	0,0	0,0
Sanidine Na0.56	0,6	0,5	0,5	0,3

Example 4 (Reference example)

In Example 4.1, the raw clay 4 was used without any limestone being added as a reference. In Examples 4.2, 4.3 and 4.4 the raw clay 4 was mixed with limestone in a ratio of 90/10, 80/20 and 60/40, respectively. The mineralogical composition of Examples 4.1, 4.2, 4.3 and 4.4 is given in Table 5. All values are given in wt.-%.

10 Table 5:

	Ex. 4.1	Ex. 4.2	Ex. 4.3	Ex. 4.4
	Raw clay 4	Raw clay 4 + BL200 (90/10)	Raw clay 4 + BL200 (80/20)	Raw clay 4 + BL200 (60/40)
Montmorillonite	0,4	0,4	0,3	0,2
Muscovite 2M1	0,3	0,2	0,2	0,2
Muscovite 2M2	0,3	0,2	0,2	0,2
Chlorite lib	1,4	1,3	1,1	0,8
Clinochlore-1MIIb	0	0	0	0
Kaolinite	47,9	43,1	38,3	28,7

Quartz	42,1	37,9	33,7	25,2
Albite	0,2	0,1	0,1	0,1
Andesine An50	0	0	0	0
Anorthite	0	0	0	0
Microcline	0,7	0,6	0,6	0,4
Hematite	2,6	2,4	2,1	1,6
Goethite	0	0	0	0
Gibbsite	0	0	0	0
Bayerite	0	0	0	0
Anatase	0,5	0,5	0,4	0,3
Calcite	0	10	20	40
Dolomite	0	0	0	0
Pyrite	0,2	0,2	0,1	0,1
Alunite	0,8	0,7	0,7	0,5
Actinolite	0	0	0	0
Illite modified	2,1	1,9	1,7	1,3
Illite-smectite	0	0	0	0
Siderite	0,3	0,2	0,2	0,2
Oligoclase An25	0	0	0	0
Sanidine Na0.56	0,3	0,3	0,3	0,2

Calcination

The mixtures of Examples 1.1 - 4.4 were put in alumina crucibles and then calcined in a laboratory kiln at 800°C for 3 hours.

Composite cement

A low carbon composite cement was prepared by mixing 50 wt.-% Portland cement (CEM I from SPLC 52.5 N), 25 wt.-% limestone (BL200 from Omya) and 25 wt.-% of the calcined material of Tables 2, 3, 4 and 5. The calcined material in each case had a particle size distribution characterized by a d_{50} of 17µm.

Compressive strength measurements

The 28 days compressive strengths were tested according to EN-196-1.

Table 6 shows the compressive strength values obtained for examples 1.1-4.4

Table 6:

Example	28d-compressive strength (Mpa)
1.1	37,2
1.2	39,9
1.3	40,8
1.4	33,7
2.1	40,4
2.2	42,0
2.3	40,0
2.4	34,6
3.1	35,3
3.2	37,0
3.3	38,7
3.4	32,5
4.1	47,4
4.2	45,7
4.3	46,0
4.4	38,9

Figure 1 shows the compressive strength for each of the
5 argillaceous raw materials used in Examples 1, 2, 3 and 4 as
a function of the ratio of the argillaceous material and the
limestone.

As can be seen from Fig. 1, in examples 1, 2 and 3 the
10 compressive strength increases when argillaceous material
with a muscovite content above 20 wt.-% is co-calcined with
limestone. In examples 1 and 3 this is true for the addition
of up to 20 wt.-% limestone, but not for the addition of
40 wt.-% limestone. In example 2, this is only true for the
15 addition of 10 wt.-% limestone. The type of clay used in
example 2 requires less limestone, because this clay
originally contains more limestone than the argillaceous
material used in examples 1 and 3.

20 On the contrary, co-calcination of clay material with
limestone results in a decrease of the compressive strength
as demonstrated in example 4, despite a high kaolinite

content of 47.9 wt.-% (Table 1), if the muscovite content is low, and in particular below the lower limit (1 wt.-%) required by the invention. The examples demonstrate that the addition of a source of calcium oxide is beneficial only if a significant content of muscovite is present in the formulation. Example 4 demonstrates that there is no beneficial effect of co-calcining clay having a muscovite content of below 1 wt.-% for having with high kaolinite content.

The invention refers to a method of producing a pozzolanic material for use in a low-carbon cement. Further, the invention refers to a hydraulic cement comprising Portland cement, an additional material and a pozzolanic material.

5

Cement production is one of the most significant sources of anthropogenic carbon dioxide (CO₂) emissions, accounting for approximately 7-8% of global CO₂ emissions. This is primarily due to the fact that the production of traditional Portland cement involves the calcination of limestone (calcium carbonate), a process that releases a significant amount of CO₂. Furthermore, the energy-intensive nature of cement production, which often involves burning fossil fuels, contributes additional CO₂ emissions.

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Low-carbon cements, also known as green or sustainable cements, have been developed to address these environmental concerns. These types of cements aim to significantly reduce the carbon footprint associated with cement production. This is achieved by altering the composition and manufacturing process of the cement, in order to decrease the amount of CO₂ produced per unit of cement produced.

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One of the main ways in which low-carbon cements achieve this reduction is by replacing some of the clinker with other materials. Examples of such substitutions include the use of industrial byproducts such as fly ash and slag, as well as naturally occurring materials like pozzolana, or calcined clays. An example of a low-carbon cement is the Limestone Calcined Clay Cement (LC3), a composite binder comprising clinker, calcined clay, limestone, and gypsum.

However, the practical implementation of low-carbon cement production based on calcined clay presents several challenges. Foremost among these is the requirement for the raw clay used to produce the calcined clay component of the cement to have a high content of kaolinite, typically no less than 40%. Unfortunately, it is not uncommon to encounter clay materials with kaolinite contents below this threshold, typically not exceeding 25%. This low percentage makes them unsuitable for the production of low-carbon cement under conventional conditions.

Kaolinite has a layered silicate structure, composed of alternating layers of tetrahedral sheets of silica and octahedral sheets of alumina linked with each other by oxygen atoms. When kaolinite is heated during the calcination process, a sequence of reactions occurs leading to the dehydroxylation (loss of water) and transformation of the kaolinite into an amorphous material known as metakaolin.

Metakaolin is highly reactive in a cementitious environment. It reacts with calcium hydroxide (produced during the hydration of Portland cement) in a process known as pozzolanic reaction, forming calcium silicate hydrates (C-S-H), calcium aluminate hydrates and calcium aluminate silicate hydrates. All these products contribute significantly to the compressive strength of the cement. They are the main binders in concrete and responsible for the strength development. The greater the volume of binders produced, the higher the compressive strength of the resulting cementitious matrix. Therefore, a higher kaolinite content, which leads to more metakaolin, allows for more binder formation and results in higher compressive strength.

Thus, the requirement for high kaolinite content in the clay used for low-carbon cement production is tied directly to the contribution of the resulting metakaolin to the mechanical performance of the cement, particularly its compressive strength. Using clay with a lower kaolinite content without compensating for the decrease in reactivity could lead to a drop in the cement's mechanical performance.

One potential solution to this problem was proposed in FR 3084665 B1. The patent suggests the use of clay with a kaolinite content of less than 25%, but with a significant amount of muscovite and/or illite, constituting at least 20%, to make a cementitious material. However, when the cementitious material produced in this manner is used in a cement formulation where the Portland cement (CEM I) component is less than 70%, the mechanical performance of the resulting composite cement suffers a significant decrease. This substantial drop in performance prevents the production of a low-clinker or low-CEM I cement with acceptable performance characteristics using such clay materials.

Therefore, the instant invention aims at enabling the production of a low-carbon cement using clay with low kaolinite content without compromising compressive strength performance.

To solve this object, the invention provides a method of producing a pozzolanic material for use in a low-carbon cement, comprising

- providing an argillaceous material that comprises 1 - 49 wt.-% kaolinite, 1 - 49 wt.-% muscovite and < 5 wt.-% calcite,

- mixing the argillaceous material with a source of calcium oxide,
- co-calcining the argillaceous material and the source of calcium oxide at a temperature of 700-900°C over a time period of 15-240 min, thereby obtaining the pozzolanic material.

The invention is based on the surprising finding that the co-calcination of a clay material having a low kaolinite content with a source of calcium oxide provides a pozzolanic material that, when used as a cementitious material in a low-carbon cement, compensates for the loss of compressive strength that would otherwise occur due to the low kaolinite content.

The combination of muscovite with a source of calcium oxide, when being co-calcined, appears to have a synergistic effect contributing to the compressive strength of the resulting cementitious material leading to improved compressive strength values despite low kaolinite content. This ensures that even clays with low kaolinite content can be effectively used in the production of low-carbon cement.

Preferably, limestone may be used as the source of calcium oxide. However, alternative sources of calcium oxide may also be used. Preferably, at least one member selected from the group consisting of steel slag, blast furnace slag, CaO rich fly ash, free lime, paper sludges, and recycled concrete fines, may be used as the source of calcium oxide. As used herein, a source of calcium oxide is considered to refer to any mineral material that contains calcium oxide or that contains a mineral phase that, upon calcination at a temperature of 700-900°C, is at least partially transformed into calcium oxide (CaO).

Preferably, the material that is used as the source of calcium oxide contains > 10 wt.-%, preferably > 20 wt.-%, of calcite, or > 5 wt.-%, preferably > 10 wt.-% of calcium oxide. In case the source of calcium oxide contains both calcite and calcium oxide, the sum of both preferably is at least 10 wt.-% of said material. Preferably, the material that is used as the source of calcium oxide contains < 15 wt.-% MgO.

The argillaceous material that is co-calcined with the source of calcium oxide may also contain calcite or calcium oxide. In this case a minimum amount of calcium oxide and/or calcite may preferably be defined based on the combined content of calcium oxide and/or calcite in the argillaceous material and the source of calcium oxide.

Preferably, the mixture of argillaceous material and the source of calcium oxide contains > 10 wt.-%, preferably 20 wt.-%, calcite. Preferably, the upper limit for the calcite content is 25 wt.-% or 20 wt.-%. Exceeding a content of 25 wt.-% or 20 wt.-% of calcite, as the case may be, could result in an excessive dilution of the reactive clay components in the mixture.

Preferably, the mixture of argillaceous material and the source of calcium oxide contains > 5 wt.-%, preferably 10 wt.-%, calcium oxide. Preferably, the upper limit for the calcium oxide content is 12.5 wt.-% or 25.5 wt.-%. Exceeding a content of 12.5 wt.-% or 25.5 wt.-% of calcium oxide, as the case may be, could result in an excessive dilution of the reactive clay components in the mixture.

According to the invention, the argillaceous material comprises 1 - 49 wt.-% kaolinite. Preferably, the argillaceous material may contain < 45 wt.-%, < 40 wt.-%, < 35 wt.-%, < 30 wt.-%, < 25 wt.-%, < 20 wt.-%, < 15 wt.-% or
5 < 10 wt.-% kaolinite. In any case, the minimum content of kaolinite in the argillaceous material preferably is 1 wt.-%, more preferably 5 wt.-%.

Preferably, the argillaceous material comprises 1-40 wt.-%
10 kaolinite, and even more preferably, the argillaceous material comprises 1-30 wt.-% kaolinite.

According to the invention the argillaceous material contains 1-49 wt.-% muscovite. Preferably, the argillaceous material
15 contains > 1 wt.-%, preferably > 10 wt.-% or > 20 wt.-% or > 30 wt.-% muscovite.

Preferably, the argillaceous material contains 10-74 wt.-% illite and/or smectite. This is understood to refer to the
20 combined content of illite and smectite if both minerals are present, or to the content of illite or smectite only, if the respective other mineral is absent.

Preferably, the argillaceous material contains 20-35 wt.-%,
25 illite and/or smectite. Other preferred ranges are characterized by a lower limit of 10, 15, 20 or 25 wt.-% and by an upper limit of 30, 40, 50 or 74 wt.-%, wherein any combination of any one of the lower limits and any one of the upper limits is disclosed herewith.

Preferably, the combined content of illite and smectite in the argillaceous material is < 50 wt.-%, preferably < 40 wt.-%,
30 %, most preferably < 30 wt.-%.

Any content of kaolinite, illite, muscovite, and calcite or any other mineral phase indicated in wt.-% is measured by XRD Rietveld method. X-ray diffraction (XRD) measurements were made of powdered samples which were hand ground to pass a 63 μm sieve. A D8 Advance X-ray Diffractometer from Bruker was used which was operated using Cu K α radiation at an acceleration voltage of 25 kV and a current of 40 mA, scanning at 2θ range of 3-65°, with 4336 steps and a counting time of 0.135 s per step, rotation of the sample. The quantification of the phases present in the samples was achieved by Rietveld refinement using Topas Academic v6 software.

The calcium oxide content is measured by X-ray Fluorescence (XRF).

According to the invention, co-calcining the argillaceous material and the source of calcium oxide is performed at a temperature of 700-900°C in order to obtain a pozzolanic material. Co-calcination at said temperature is carried out in order to have the kaolinite component of the argillaceous material at least partially transform to metakaolin.

Preferably, the co-calcination step is carried out so that at least 70 wt.-% of the kaolinite has completely transformed into metakaolin. In the present invention, the co-calcination of the argillaceous material and the source of calcium oxide must not be done at a temperature above 900°C as this would like to the production of a dead-burnt material that has less pozzolanic reactivity. Preferably, the co-calcination step is carried out at a temperature of 700-900°C over a time period of 15-240 minutes, preferably at a temperature of 700-900°C

over a time period of 15-180 minutes, even more preferably at a temperature of 700-900°C over a time period of 60-180 min.

Several prior art methods may be used for calcining the mixture of the argillaceous material and the source of calcium oxide, with the choice of the method being determined by factors such as the scale of production, the specific nature of the raw materials, and the desired characteristics of the final product.

According to one alternative a rotary kiln calcination is carried out. This involves feeding the mixture of argillaceous material and the source of calcium oxide into a rotating cylindrical furnace, where it is heated to the desired temperature range of 700-900°C. The rotation of the kiln ensures thorough mixing and even heating of the material, promoting consistent and efficient decarbonation of the calcium oxide source, such as limestone, and dehydroxylation of the clay minerals.

Alternatively, a vertical shaft kiln may be used for calcination. The mixture is loaded at the top of a tall, vertical furnace and heated as it descends through the kiln, undergoing the necessary chemical transformations.

Alternatively, a fluidized bed calcination may be used, which is a method wherein the mixture is suspended in a rising flow of hot gas. This ensures very high heat and mass transfer rates, providing rapid, uniform calcination.

Any type of argillaceous material may be used that contains the amounts of kaolinite, illite and muscovite indicated above. The argillaceous material may for example be a clay

material or a shale material. The main components of shale are clay minerals, quartz and calcite.

The argillaceous material may comprise any of the following mineral components, in addition to kaolinite and illite and/or muscovite: quartz (up to 49 wt.-%), dolomite, albite, chlorite, microcline and calcite.

According to a preferred embodiment of the invention, the argillaceous material, before being subjected to the step of co-calcining, is ground to a particle size characterized by a $D_{90} < 200\mu\text{m}$, preferably $< 100\mu\text{m}$. This enhanced surface area facilitates more efficient heat transfer and chemical interactions during the co-calcination process, leading to more effective dehydroxylation of clay minerals and decarbonation of the calcium source.

The D_{90} corresponds to the 90th centile of the volume distribution of particle sizes, i.e. 90% of the volume consists of particles for which the size is less than the measured value. The D_{90} of particles is generally determined by laser diffraction. The particle size distribution of the different powders are obtained with a laser Malvern MS2000 granulometer. The measurement is carried out in a suitable medium (for example, in an aqueous medium); the size of the particles should be comprised between $0.02\mu\text{m}$ and 2mm . The light source consists of a red He-Ne laser (632nm) and a blue diode (466nm). The optical model is the Fraunhofer one, the computation matrix is of the polydisperse type.

A measurement of background noise is first of all carried out with a pump rate of 2,000 rpm, a stirring rate of 800 rpm and a measurement of noise over 10 s, in the absence of

ultrasonic waves. It is then checked that the light intensity of the laser is at least equal to 80%, and that a decreasing exponential curve is obtained for the background noise. If this is not the case, the lenses of the cell have to be
5 cleaned. A first measurement is then carried out on the sample with the following parameters: pump rate of 2,000 rpm, stirring rate of 800 rpm, absence of ultrasonic waves, obscuration limit between 10 and 20%. The sample is introduced in order to have an obscuration slightly greater
10 than 10%. After stabilization of the obscuration, the measurement is carried out with a duration between the immersion and the measurement set to 10 s. The measurement duration is of 30 s (30,000 analyzed diffraction images). In the obtained granulogram, the fact that a portion of the
15 population of the powder may be agglomerated should be taken into account.

Next, a second measurement (without emptying the tank) is carried out with ultrasonic waves. The pump rate is brought
20 to 2,500 rpm, the stirring to 1,000 rpm, the ultrasonic waves are 100 % emitted (30 Watts). This rate is maintained for 3 minutes, and then one returns to the initial parameters: pump rate 2,000 rpm, stirrer rate of 800 rpm, absence of ultrasonic waves. After 10 s (for removing the possible air
25 bubbles), a measurement is made for 30 s (30,000 analyzed images). This second measurement corresponds to a powder de-agglomerated by ultrasonic dispersion. Each measurement is repeated least twice in order to check the stability of the result. The apparatus is calibrated before each working
30 session by means of a standard sample (silica C10 Sifraco) the grain size curve of which is known. All the measurements shown in the description and the announced ranges correspond to the values obtained with ultrasonic waves.

Particle size reduction also ensures the uniformity of the mixture with the calcium oxide source. This homogeneity fosters even heating and consistent chemical reactions during co-calcination, which translates into a more predictable and controlled quality of the final product. The small particle size also enables better incorporation of the calcined product within the cement matrix, thus enhancing the mechanical properties of the resulting cement, such as strength and durability.

According to another preferred embodiment, the argillaceous material may be dried before being subjected to the grinding step. Drying may be performed at a temperature of 90-120, preferably 100-110°C.

The step of mixing the argillaceous material with the source of calcium oxide may be performed in any suitable mixing device. Preferably, the mixing step may be conducted in a grinding device, such as in a ball mill. The mixture of the argillaceous material and the source of calcium oxide may be ground to a fineness characterised by a $D_{90} < 200 \mu\text{m}$, preferably $D_{90} < 100 \mu\text{m}$. By reducing the particle size, the total surface area of the material available for reactions during co-calcination significantly increases. This enhanced surface area facilitates more efficient heat transfer and chemical interactions during the co-calcination process, leading to more effective dehydroxylation of clay minerals and decarbonation of the calcium source.

30

The ratio of the argillaceous material and the source of calcium oxide preferably is in the range of 95/5 - 70/30 (w/w), preferably 90/10 - 75/25 (w/w).

According to a preferred embodiment, the ratio of the argillaceous material and the source of calcium oxide is selected so that the mixture of argillaceous material and the source of calcium oxide contains > 5 wt.-%, preferably 10-25 wt.-% or 10-20 wt.-%, calcium oxide.

According to a second aspect, the invention provides a hydraulic cement, comprising 45-70 wt.-% Portland cement, an additional material selected from the group consisting of ground granulated blast-furnace slag, silica fume, natural pozzolana, siliceous fly ash, calcareous fly ash, burnt shale and limestone, and a pozzolanic material obtained by a method according to the first aspect of the invention. Hence, a low-carbon cement is provided that has a reduced clinker content and that, due to the presence of the pozzolanic material of the invention, still has an acceptable compressive strength. In particular, the hydraulic cement of the invention has an improved compressive strength when compared to a reference cement that comprises the same amount of calcined alumino silicate material, but without the addition of a source of calcium oxide.

Preferably, the hydraulic cement may comprise 45-60 wt.-%, preferably 45-50 wt.-%, Portland cement. The term "Portland cement", also referred to as "Ordinary Portland Cement (OPC)", refers to a type of hydraulic cement that sets, hardens, and adheres to other materials to bind them together. The primary components of Portland cement are calcium, silicon, aluminum, and iron, which are typically derived from limestone, clay, and other natural materials. These materials are crushed, combined, and heated in a kiln to a high temperature to produce clinker. This clinker is

then ground into a fine powder, often with a small amount of gypsum added to control the setting time of the final product.

5 Therefore, the Portland cement preferably is a cement of the type "CEM I", as defined in European standard EN 197-1:2011. It consists of 95-100% Portland cement clinker and up to 5% of a minor additional constituent, such as limestone or gypsum, that enhances the properties or the workability of
10 the cement.

Preferably, the hydraulic cement of the invention is a cement of the type CEM II/C-M, as defined in European standard NF EN 197-5:2021. This type of cement is defined by a Portland
15 cement content of 50-64 wt.-%, a combined content of the additional material and the pozzolanic material of 36-50 wt.-% and an optional content of minor additional constituents (0-5 wt.-%).

20 According to a preferred embodiment of the invention, the additional material is limestone.

Preferably, the hydraulic cement of the invention is a cement of the type CEM II/C-M (Q-LL), as defined in European
25 standard EN 197-5:2021. This type of cement is defined by a Portland cement content of 50-64 wt.-% and a combined content of limestone and the pozzolanic material of 36-50 wt.-%.

Preferably, the hydraulic cement of the invention comprises
30 15-30 wt.-% of the additional material, in particular limestone.

Preferably, the hydraulic cement of the invention comprises 15-30 wt.-% of the pozzolanic material.

Preferably, the combined amount of the additional material and the pozzolanic material is < 50 wt.-%, preferably 30-50 wt.-%.

As used herein, any content of Portland cement, the additional material and the pozzolanic material given in wt.-% is based on the total weight of the hydraulic cement.

In the following, the invention will be described in more detail with reference to the following examples.

Four different sources of argillaceous material were used as a raw material for preparing a pozzolanic material. Table 1 indicates the mineral composition of the raw materials according to Examples 1-4. All values are given in wt.-%. The mineralogical composition of the materials was measured by the XRD Rietveld method. The Rwp (weighted profile R value) given in the last line of Table 1 is the value that indicates how good or bad the predicted fitting is as compared to the experimental setting. The lower this value the better the prediction.

Table 1:

	Ex.1	Ex.2	Ex.3	Ex.4
	Raw clay 1	Raw clay 2	Raw clay 3	Raw clay 4
Montmorillonite	0	0	0	0,4
Muscovite 2M1	18	20	21	0,3
Muscovite 2M2	4	3,5	3,2	0,3
Chlorite lib	4	4,6	2,2	1,4
Clinocllore-1Mlib	0	0,0	0,0	0,0
Kaolinite	18	18,5	5,9	47,9
Quartz	33	19,3	38,6	42,1
Albite	2	3,4	0,6	0,2

Andesine An50	0	0,0	0,0	0,0
Anorthite	0	0,0	0,0	0,0
Microcline	3	4,2	9,3	0,7
Hematite	1	0,5	0,4	2,6
Goethite	0	0,0	0,0	0,0
Gibbsite	0	0,0	0,0	0,0
Bayerite	0	0,0	0,0	0,0
Anatase	0	0,1	0,1	0,5
Calcite	0	2,7	0,2	0,0
Dolomite	0	7,3	8,9	0,0
Pyrite	0	0,0	1,2	0,2
Alunite	1	0,6	0,3	0,8
Actinolite	0	0,0	0,0	0,0
Illite modified	7	7,1	4,5	2,1
Illite-smectite	8	6,6	2,9	0,0
Siderite	0	0,5	0,2	0,3
Oligoclase An25	1	1,2	0,0	0,0
Sanidine Na0.56	1	0,2	0,6	0,3
Rwp	8	7	8	10

In all examples, the argillaceous raw material was dried at 105°C and then ground until a particle diameter $d_{90} < 200 \mu\text{m}$. Subsequently, the argillaceous raw material was mixed with limestone, i.e. the product "BL200" supplied by Omya, consisting of 100 wt.-% calcite (CaCO_3). Mixing was carried out in a planetary ball mill PM 400 from Retsch for less than 10 minutes.

10 Example 1

The raw clay 1 of Example 1 and limestone were used in different mixing ratios. In Example 1.1, the raw clay 1 was used without any limestone being added as a reference example. In Examples 1.2, 1.3 and 1.4 the raw clay 1 was mixed with limestone in a ratio of 90/10, 80/20 and 60/40, respectively. The mineralogical composition of Examples 1.1, 1.2, 1.3 and 1.4 is given in Table 2. All values are given in wt.-%.

20 Table 2:

	Ex. 1.1	Ex. 1.2	Ex. 1.3	Ex. 1.4
	Raw clay 1	Raw clay 1 + BL200 (90/10)	Raw clay 1 + BL200 (80/20)	Raw clay 1 + BL200 (60/40)
Montmorillonite	0,0	0,0	0,0	0,0
Muscovite 2M1	18,4	16,1	14,3	10,7
Muscovite 2M2	4,1	3,9	3,5	2,6
Chlorite lib	3,9	3,9	3,5	2,6
Clinochlore-1Mlib	0,0	0,0	0,0	0,0
Kaolinite	18,0	16,5	14,6	11,0
Quartz	32,8	29,1	25,8	19,4
Albite	1,8	1,8	1,6	1,2
Andesine An50	0,0	0,0	0,0	0,0
Anorthite	0,0	0,0	0,0	0,0
Microcline	2,6	2,0	1,7	1,3
Hematite	0,6	0,5	0,4	0,3
Goethite	0,0	0,0	0,0	0,0
Gibbsite	0,0	0,0	0,0	0,0
Bayerite	0,0	0,0	0,0	0,0
Anatase	0,0	0,0	0,0	0,0
Calcite	0,1	10,0	19,9	39,8
Dolomite	0,2	0,0	0,0	0,0
Pyrite	0,3	0,0	0,0	0,0
Alunite	0,7	0,6	0,6	0,4
Actinolite	0,0	0,0	0,0	0,0
Illite modified	6,9	6,2	5,5	4,2
Illite-smectite	7,6	7,3	6,5	4,9
Siderite	0,3	0,0	0,0	0,0
Oligoclase An25	0,9	0,8	0,7	0,5
Sanidine Na0.56	0,6	0,5	0,5	0,3

Example 2

In Example 2.1, the raw clay 2 was used without any limestone being added as a reference example. In Examples 2.2, 2.3 and 2.4 the raw clay 2 was mixed with limestone in a ratio of 90/10, 80/20 and 60/40, respectively. The mineralogical composition of Examples 2.1, 2.2, 2.3 and 2.4 is given in Table 3. All values are given in wt.-%.

Table 3:

	Ex. 2.1	Ex. 2.2	Ex. 2.3	Ex. 2.4
	Raw clay 2	Raw clay 2 + BL200 (90/10)	Raw clay 2 + BL200 (80/20)	Raw clay 2 + BL200 (60/40)

Montmorillonite	0,0	0,0	0,0	0,0
Muscovite 2M1	19,8	19,6	17,4	13,1
Muscovite 2M2	3,5	2,5	2,2	1,7
Chlorite lib	4,6	4,7	4,2	3,1
Clinochlore-1Mlib	0,0	0,0	0,0	0,0
Kaolinite	18,5	15,6	13,9	10,4
Quartz	19,3	17,8	15,8	11,9
Albite	3,4	3,6	3,2	2,4
Andesine An50	0,0	0,0	0,0	0,0
Anorthite	0,0	0,0	0,0	0,0
Microcline	4,2	3,8	3,4	2,5
Hematite	0,5	0,5	0,4	0,3
Goethite	0,0	0,0	0,0	0,0
Gibbsite	0,0	0,0	0,0	0,0
Bayerite	0,0	0,0	0,0	0,0
Anatase	0,1	0,3	0,3	0,2
Calcite	2,7	11,9	21,7	41,1
Dolomite	7,3	5,9	5,3	3,9
Pyrite	0,0	0,0	0,0	0,0
Alunite	0,6	0,4	0,4	0,0
Actinolite	0,0	0,0	0,0	0,0
Illite modified	7,1	6,1	5,4	4,1
Illite-smectite	6,6	5,7	5,1	3,8
Siderite	0,5	0,4	0,3	0,3
Oligoclase An25	1,2	1,1	1,0	0,7
Sanidine Na0.56	0,2	0,0	0,0	0,0

Example 3

In Example 3.1, the raw clay 3 was used without any limestone being added as a reference example. In Examples 3.2, 3.3 and 3.4 the raw clay 3 was mixed with limestone in a ratio of 90/10, 80/20 and 60/40, respectively. The mineralogical composition of Examples 3.1, 3.2, 3.3 and 3.4 is given in Table 4. All values are given in wt.-%.

Table 4:

	Ex. 3.1	Ex. 3.2	Ex. 3.3	Ex. 3.4
	Raw clay 3	Raw clay 3 + BL200 (90/10)	Raw clay 3 + BL200 (80/20)	Raw clay 3 + BL200 (60/40)
Montmorillonite	0,0	0,0	0,0	0,0
Muscovite 2M1	21,0	18,9	16,8	12,6
Muscovite 2M2	3,2	2,8	2,5	1,9

Chlorite lib	2,2	2,0	1,8	1,3
Clinochlore-1Mlib	0,0	0,0	0,0	0,0
Kaolinite	5,9	5,3	4,7	3,6
Quartz	38,6	34,7	30,9	23,1
Albite	0,6	0,5	0,5	0,3
Andesine An50	0,0	0,0	0,0	0,0
Anorthite	0,0	0,0	0,0	0,0
Microcline	9,3	8,4	7,5	5,6
Hematite	0,4	0,3	0,3	0,2
Goethite	0,0	0,0	0,0	0,0
Gibbsite	0,0	0,0	0,0	0,0
Bayerite	0,0	0,0	0,0	0,0
Anatase	0,1	0,1	0,1	0,1
Calcite	0,2	10,1	20,1	39,9
Dolomite	8,9	8,0	7,1	5,3
Pyrite	1,2	1,1	1,0	0,7
Alunite	0,3	0,3	0,3	0,2
Actinolite	0,0	0,0	0,0	0,0
Illite modified	4,5	4,1	3,6	2,7
Illite-smectite	2,9	2,6	2,3	1,7
Siderite	0,2	0,2	0,1	0,1
Oligoclase An25	0,0	0,0	0,0	0,0
Sanidine Na0.56	0,6	0,5	0,5	0,3

Example 4 (Reference example)

In Example 4.1, the raw clay 4 was used without any limestone being added as a reference. In Examples 4.2, 4.3 and 4.4 the raw clay 4 was mixed with limestone in a ratio of 90/10, 80/20 and 60/40, respectively. The mineralogical composition of Examples 4.1, 4.2, 4.3 and 4.4 is given in Table 5. All values are given in wt.-%.

Table 5:

	Ex. 4.1	Ex. 4.2	Ex. 4.3	Ex. 4.4
	Raw clay 4	Raw clay 4 + BL200 (90/10)	Raw clay 4 + BL200 (80/20)	Raw clay 4 + BL200 (60/40)
Montmorillonite	0,4	0,4	0,3	0,2
Muscovite 2M1	0,3	0,2	0,2	0,2
Muscovite 2M2	0,3	0,2	0,2	0,2
Chlorite lib	1,4	1,3	1,1	0,8
Clinochlore-1Mlib	0	0	0	0
Kaolinite	47,9	43,1	38,3	28,7

Quartz	42,1	37,9	33,7	25,2
Albite	0,2	0,1	0,1	0,1
Andesine An50	0	0	0	0
Anorthite	0	0	0	0
Microcline	0,7	0,6	0,6	0,4
Hematite	2,6	2,4	2,1	1,6
Goethite	0	0	0	0
Gibbsite	0	0	0	0
Bayerite	0	0	0	0
Anatase	0,5	0,5	0,4	0,3
Calcite	0	10	20	40
Dolomite	0	0	0	0
Pyrite	0,2	0,2	0,1	0,1
Alunite	0,8	0,7	0,7	0,5
Actinolite	0	0	0	0
Illite modified	2,1	1,9	1,7	1,3
Illite-smectite	0	0	0	0
Siderite	0,3	0,2	0,2	0,2
Oligoclase An25	0	0	0	0
Sanidine Na0.56	0,3	0,3	0,3	0,2

Calcination

The mixtures of Examples 1.1 - 4.4 were put in alumina crucibles and then calcined in a laboratory kiln at 800°C for 3 hours.

Composite cement

A low carbon composite cement was prepared by mixing 50 wt.-% Portland cement (CEM I from SPLC 52.5 N), 25 wt.-% limestone (BL200 from Omya) and 25 wt.-% of the calcined material of Tables 2, 3, 4 and 5. The calcined material in each case had a particle size distribution characterized by a d_{50} of 17µm.

Compressive strength measurements

The 28 days compressive strengths were tested according to EN-196-1.

Table 6 shows the compressive strength values obtained for examples 1.1-4.4

Table 6:

Example	28d-compressive strength (Mpa)
1.1	37,2
1.2	39,9
1.3	40,8
1.4	33,7
2.1	40,4
2.2	42,0
2.3	40,0
2.4	34,6
3.1	35,3
3.2	37,0
3.3	38,7
3.4	32,5
4.1	47,4
4.2	45,7
4.3	46,0
4.4	38,9

Figure 1 shows the compressive strength for each of the
 5 argillaceous raw materials used in Examples 1, 2, 3 and 4 as
 a function of the ratio of the argillaceous material and the
 limestone.

As can be seen from Fig. 1, in examples 1, 2 and 3 the
 10 compressive strength increases when argillaceous material
 with a muscovite content above 20 wt.-% is co-calcined with
 limestone. In examples 1 and 3 this is true for the addition
 of up to 20 wt.-% limestone, but not for the addition of
 40 wt.-% limestone. In example 2, this is only true for the
 15 addition of 10 wt.-% limestone. The type of clay used in
 example 2 requires less limestone, because this clay
 originally contains more limestone than the argillaceous
 material used in examples 1 and 3.

20 On the contrary, co-calcination of clay material with
 limestone results in a decrease of the compressive strength
 as demonstrated in example 4, despite a high kaolinite

content of 47.9 wt.-% (Table 1), if the muscovite content is low, and in particular below the lower limit (1 wt.-%) required by the invention. The examples demonstrate that the addition of a source of calcium oxide is beneficial only if a significant content of muscovite is present in the formulation. Example 4 demonstrates that there is no beneficial effect of co-calcining clay having a muscovite content of below 1 wt.-% for having with high kaolinite content.

Claims:

1. A method of producing a pozzolanic material for use in a low-carbon cement, comprising
 - 5 - providing an argillaceous material that comprises 1 - 49 wt.-% kaolinite, 1 - 49 wt.-% muscovite and < 5 wt.-% calcite,
 - mixing the argillaceous material with a source of calcium oxide,
 - 10 - co-calcining the argillaceous material and the source of calcium oxide at a temperature of 700-900°C over a time period of 15-240 min, thereby obtaining the pozzolanic material.
- 15 2. Method according to claim 1, wherein limestone containing < 15 wt.-% MgO is used as the only source of calcium oxide, and where no free calcium oxide is present in the limestone.
- 20 3. Method according to claim 1, wherein at least one member selected from the group consisting of steel slag, blast furnace slag, CaO rich fly ash, free lime, paper sludges, and recycled concrete fines, is used as the source of calcium oxide.
- 25 4. Method according to claim 1, 2 or 3, wherein the argillaceous material and the source of calcium oxide, before being subjected to the step of co-calcining, are ground to a particle size characterized by a $d_{90} < 200\mu\text{m}$, preferably $d_{90} <$
30 100 μm .

5. Method according to any one of claims 1 to 4, wherein the argillaceous material comprises < 30 wt.-%, preferably < 25 wt.-% or < 20 wt.-% kaolinite.
- 5 6. Method according to claim 2, 4 or 5, wherein the mixture of argillaceous material and the source of calcium oxide contains > 10 wt.-%, preferably > 20 wt.-%, calcite.
7. Method according to claim 3, 4 or 5, wherein the mixture
10 of argillaceous material and the source of calcium oxide contains > 5 wt.-%, preferably > 20 wt.-%, calcium oxide.
8. Method according to any one of claims 1 to 7, wherein the combined content of kaolinite, illite and muscovite in
15 the argillaceous material is > 30 wt.-%, > 35 wt.-%, > 40 wt.-% or > 45 wt.-%.
9. Method according to any one of claims 1 to 8, wherein the argillaceous material and the source of calcium oxide is
20 in the range of 95/5 - 70/30 (w/w), preferably 90/10 - 75/25 (w/w).
10. Method according to claim 9, wherein the ratio is selected so that the mixture of argillaceous material and the
25 source of calcium oxide contains > 5 wt.-%, preferably 10-25 wt.-% or 10-20 wt.-%, calcium oxide .
11. A hydraulic cement, comprising:
- a) 45-70 wt.-% Portland cement,
- 30 b) an additional material selected from the group consisting of ground granulated blast-furnace slag, silica fume, natural pozzolana, siliceous fly ash, calcareous fly ash, burnt shale and limestone, and recycled concrete fines.

c) a pozzolanic material obtained by a method according to any one of claims 1 to 10.

12. Hydraulic cement according to claim 11, wherein the
5 additional material is limestone.

13. Hydraulic cement according to claim 11 or 12, comprising
15-30 wt.-% of the additional material.

10 14. Hydraulic cement according to claim 11, 12 or 13,
comprising 45-60 wt.-%, preferably 45-50 wt.-%, Portland
cement.

15 15. Hydraulic cement according to any one of claims 11 to
14, wherein the Portland cement is a cement of the type CEM
I, as defined in European standard EN 197-1:2011.

16. Hydraulic cement according to any one of claims 11 to
15, comprising 15-30 wt.-% of the pozzolanic material.

20

17. Hydraulic cement according to any one of claims 11 to
16, wherein the combined amount of the additional material
and the pozzolanic material is < 50 wt.-%, preferably 30-
50 wt.-%.

25

Claims:

1. A method of producing a pozzolanic material for use in a low-carbon cement, comprising
 - 5 - providing an argillaceous material that comprises 1 - 49 wt.-% kaolinite, 1 - 49 wt.-% muscovite and < 5 wt.-% calcite,
 - mixing the argillaceous material with a source of calcium oxide,
 - 10 - co-calcining the argillaceous material and the source of calcium oxide at a temperature of 700-900°C over a time period of 15-240 min, thereby obtaining the pozzolanic material.
- 15 2. Method according to claim 1, wherein limestone containing < 15 wt.-% MgO is used as the only source of calcium oxide, and where no free calcium oxide is present in the limestone.
- 20 3. Method according to claim 1, wherein at least one member selected from the group consisting of steel slag, blast furnace slag, CaO rich fly ash, free lime, paper sludges, and recycled concrete fines, is used as the source of calcium oxide.
- 25 4. Method according to claim 1, 2 or 3, wherein the argillaceous material and the source of calcium oxide, before being subjected to the step of co-calcining, are ground to a particle size characterized by a $d_{90} < 200\mu\text{m}$, preferably $d_{90} <$
30 $100\mu\text{m}$.

5. Method according to any one of claims 1 to 4, wherein the argillaceous material comprises < 30 wt.-%, preferably < 25 wt.-% or < 20 wt.-% kaolinite.

5 6. Method according to claim 2, 4 or 5, wherein the mixture of argillaceous material and the source of calcium oxide contains > 10 wt.-%, preferably > 20 wt.-%, calcite.

7. Method according to claim 3, 4 or 5, wherein the mixture
10 of argillaceous material and the source of calcium oxide contains > 5 wt.-%, preferably > 20 wt.-%, calcium oxide.

8. Method according to any one of claims 1 to 7, wherein the combined content of kaolinite, illite and muscovite in
15 the argillaceous material is > 30 wt.-%, > 35 wt.-%, > 40 wt.-% or > 45 wt.-%.

9. Method according to any one of claims 1 to 8, wherein the argillaceous material and the source of calcium oxide is
20 in the range of 95/5 - 70/30 (w/w), preferably 90/10 - 75/25 (w/w).

10. Method according to claim 9, wherein the ratio is selected so that the mixture of argillaceous material and the
25 source of calcium oxide contains > 5 wt.-%, preferably 10-25 wt.-% or 10-20 wt.-%, calcium oxide .

11. A hydraulic cement, comprising:

- 30 a) 45-70 wt.-% Portland cement,
b) an additional material selected from the group consisting of ground granulated blast-furnace slag, silica fume, natural pozzolana, siliceous fly ash, calcareous fly ash, burnt shale and limestone, and recycled concrete fines.

c) a pozzolanic material obtained by a method according to any one of claims 1 to 10.

12. Hydraulic cement according to claim 11, wherein the
5 additional material is limestone.

13. Hydraulic cement according to claim 11 or 12, comprising
15-30 wt.-% of the additional material.

10 14. Hydraulic cement according to claim 11, 12 or 13,
comprising 45-60 wt.-%, preferably 45-50 wt.-%, Portland
cement.

15 15. Hydraulic cement according to any one of claims 11 to
14, wherein the Portland cement is a cement of the type CEM
I, as defined in European standard EN 197-1:2011.

16. Hydraulic cement according to any one of claims 11 to
15, comprising 15-30 wt.-% of the pozzolanic material.

20

17. Hydraulic cement according to any one of claims 11 to
16, wherein the combined amount of the additional material
and the pozzolanic material is < 50 wt.-%, preferably 30-
50 wt.-%.

25

Abstract:

Method of producing a pozzolanic material for use in a low-carbon cement

5

A method of producing a pozzolanic material for use in a low-carbon cement, comprising

- providing an argillaceous material that comprises
1 - 49 wt.-% kaolinite, 1 - 49 wt.-% muscovite and < 5 wt.-%
10 calcite,
- mixing the argillaceous material with a source of
calcium oxide,
- co-calcining the argillaceous material and the source of
calcium oxide at a temperature of 700-900°C over a time
15 period of 15-240 min, thereby obtaining the pozzolanic
material.

Fig. 1

Abstract:

Method of producing a pozzolanic material for use in a low-carbon cement

5

A method of producing a pozzolanic material for use in a low-carbon cement, comprising

- providing an argillaceous material that comprises
1 - 49 wt.-% kaolinite, 1 - 49 wt.% muscovite and < 5 wt.-%

10

calcite,

- mixing the argillaceous material with a source of
calcium oxide,

- co-calcining the argillaceous material and the source of
calcium oxide at a temperature of 700-900°C over a time

15

period of 15-240 min, thereby obtaining the pozzolanic
material.

Fig. 1

1/1

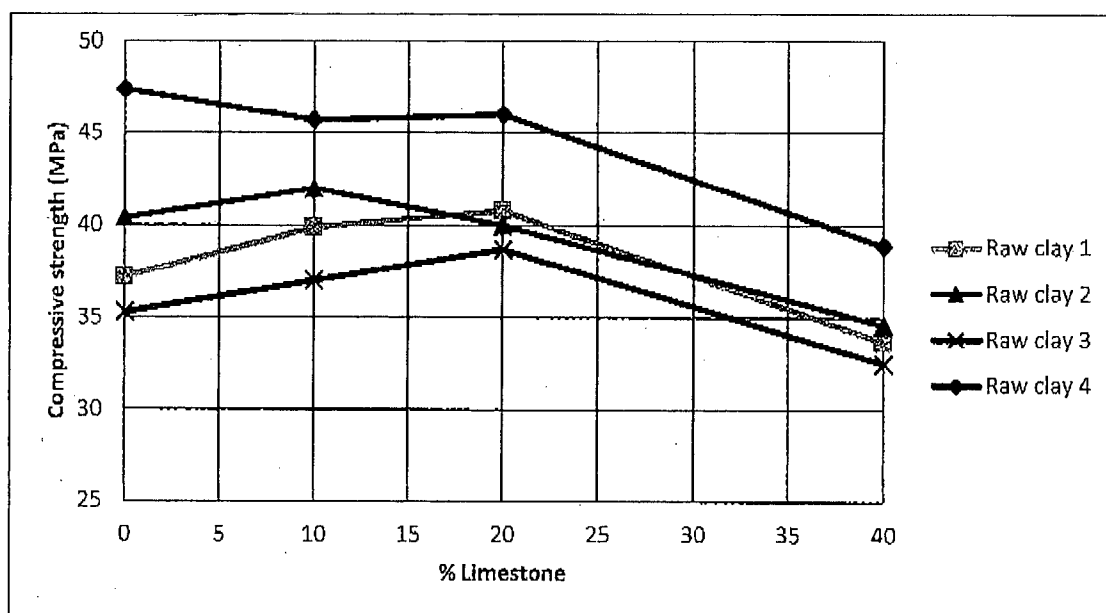


Fig. 1

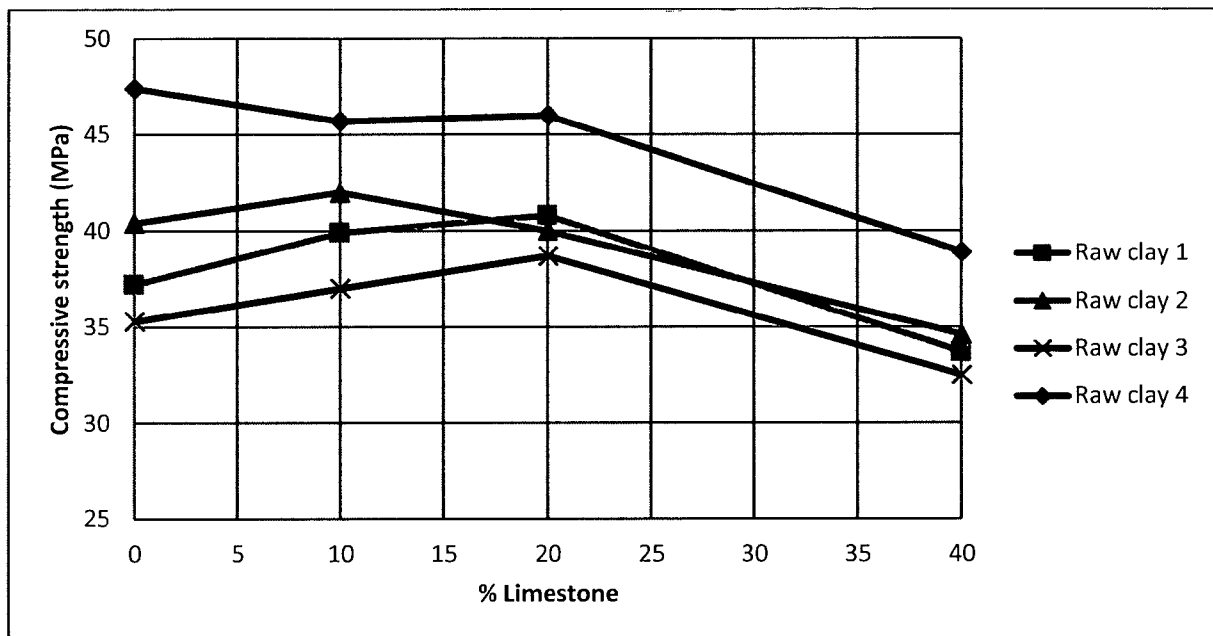


Fig. 1