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(71) Applicants: SABANCI ÜNİVERSİTESİ [TR/TR]; Orta mah. Üniversite Cad. No:27, 34956 Tuzla/Istanbul (TR). AKCANS A CEMENTO SANAYİ VE TİCARET A.S. [TR/TR]; Barbaros Mahallesi Kardelen Sokak No:2 D.124-125 Palladium Tower, 34746 Ataşehir/Istanbul (TR).

(72) Inventors: GÜLGÜN, Mehmet Ali; Sabancı Üniversitesi, Orta Mah. Üniversite Cad. No:27, 34956 Tuzla/Istanbul (TR). MOKHTARI, Pozhhan; Sabancı Üniversitesi, Or-

ta Mah. Üniversite Cad. No:27, 34956 Tuzla/Istanbul (TR). SEMASARI PARAPARI, Sorour; Sabancı Üniversitesi, Orta Mah. Üniversite Cad. No:27, 34956 Tuzla/Istanbul (TR). HASSANNEZHAD, Kosar; Sabancı Üniversitesi, Orta Mah. Üniversite Cad. No:27, 34956 Tuzla/Istanbul (TR). DÖNMEZ, Sezen; Sabancı Üniversitesi, Orta Mah. Üniversite Cad. No:27, 34956 Tuzla/Istanbul (TR). AKYOL, Yasemin; Sabancı Üniversitesi, Orta Mah. Üniversite Cad. No:27, 34956 Tuzla/Istanbul (TR). COVELLO, Gilles; Akcansa Cimento Sanayi Ve Ticaret A.S., Barbaros Mahallesi Kardelen Sokak No:2 D.124-125 Palladium Tower, 34746 Ataşehir/Istanbul (TR). GÖKALP, İsmail; Akcansa Cimento Sanayi Ve Ticaret A.S., Barbaros Mahallesi Kardelen Sokak No:2 D.124-125 Palladium Tower, 34746 Ataşehir/Istanbul (TR). ERENOĞLU, Toman; Akcansa Cimento Sanayi Ve Ticaret A.S., Barbaros Mahallesi Kardelen Sokak No:2 D.124-125 Palladium Tower, 34746 Ataşehir/Istanbul (TR). BİRİNCİ, Emre; Akcansa Cimento Sanayi Ve Ticaret A.S., Barbaros Mahallesi

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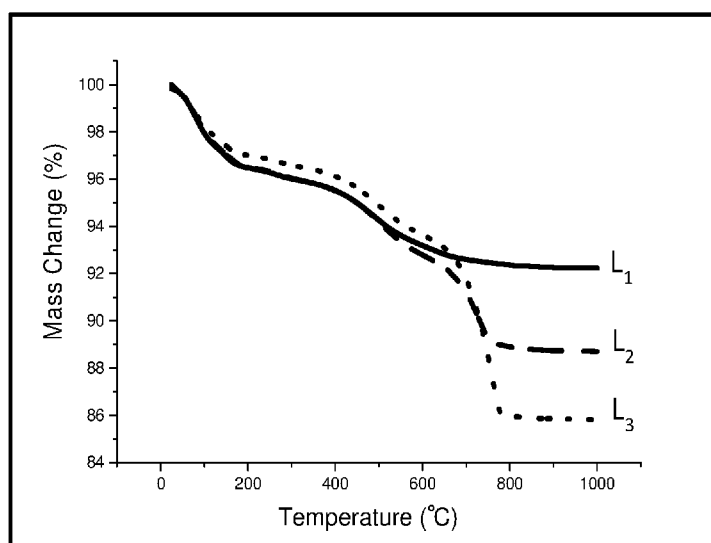


FIG.1

(57) Abstract: The present invention proposes a novel supplementary cementitious material comprising an activated mixture having at least an activated clay-based material and an activated calcium-based material. Said activated mixture is obtained by subjecting a mixture of at least a clay-based material and a calcium-based material together into an activation treatment till 70-95 % of said calcium-based material is activated; wherein amount of the clay-based material in said mixture is minimum 70% by weight of said mixture, where said clay-based material contains clay source of at least 40% by weight; and amount of the calcium-based material in said mixture is between 10-30% by weight of said mixture, where said calcium-based material contains calcium source of at least 50 % by weight. The invention further proposes a method for producing SCM and a binder containing a mixture of said novel SCM with cement.





Kardelen Sokak No:2 D.124-125 Palladium Tower, 34746 Atasehir/Istanbul (TR). **GEVEN, Caglar**; Akcansa Cimento Sanayi Ve Ticaret A.S., Barbaros Mahallesi Kardelen Sokak No:2 D.124-125 Palladium Tower, 34746 Atasehir/Istanbul (TR). **ÜSTÜN, Abdullah Özgür**; Akcansa Cimento Sanayi Ve Ticaret A.S., Barbaros Mahallesi Kardelen Sokak No:2 D.124-125 Palladium Tower, 34746 Atasehir/Istanbul (TR).

(74) **Agent: SEVINC, Erkan**; Istanbul Patent A.S., Plaza-33 Buyukdere Cad. 33/16, 34381 Sisli/Istanbul (TR).

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A NOVEL SUPPLEMENTARY CEMENTITIOUS MATERIAL AND PRODUCTION METHOD THEREOF

Technical Field of the Invention

- 5 The present invention relates to a novel supplementary cementitious material (SCM) mainly comprising an activated mixture having at least an activated clay-based material and an activated calcium-based material, a method for producing the same and binders containing a mixture of said novel SCM with cement, optionally ordinary Portland cement (OPC).

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Background of the Invention

- Cement is the main component of concrete and important for increasing durability of concrete. According to the World Business Council for Sustainable Development (WBCSD), concrete is the most widely used material on earth after water. However
15 this industrial activity comes with a heavy environmental burden. It is known that more than 5% of world carbon dioxide (CO₂) emission is coming from cement industry alone. This greenhouse gas is emitted during cement production by fossil fuel combustion and also by conversion of limestone (CaCO₃) to lime (CaO) during high temperature reactions of clinker production. The cement industry has already
20 reached significant reductions in the CO₂ emissions associated with cement production. This is done over the increased energy efficiency, use of alternative fuels including a wide range of wastes and through partial replacement of Portland cement by using SCM which requires less energy to produce than clinkers. These efforts need to be further followed to cope with the increasing demand for the
25 cement. The most suitable path to achieve sustainability in cement production is the reduction of the clinker factor by adding Supplementary Cementitious Materials (SCM). Particularly, the rate of SCMs use as partial replacements for Portland cement clinker needs to be increased.

- 30 Replacement of clinker by common SCMs such as blast furnace slag, fly ash, silica fume and natural pozzolans is already an industrial practice for composite cement. However, these materials do not meet the demand for cement due to their limited

availability as they are not obtained locally. Furthermore, their efficiency is low as a result of their high inert silica (SiO_2) content. The scarcity of common SCMs has prompted the use of calcined clays as an alternative. Clay minerals are preferable to use as SCM, since they have pozzolanic characteristics after being activated by a heat treatment process. Studies have demonstrated that efficiency and pozzolanic reactivity of the calcined clays are highly dependent on the type of the clay. Furthermore the range of calcination temperature applied during heating and cooling process also affects the efficiency of clays. Accordingly, it was noted that mineralogical purity of clays are important and activated clay can only be used as an efficient SCM if it has a high mineralogical purity (i.e., high-grade clay). Although the existence of clays is common on the earth crust in many places, the applicable and commercially useable high-grade clay deposits are relatively few. In general, clays rarely occur in nature as pure deposits but rather as mixtures of clays and non-clay minerals such as carbonates, feldspars and quartz. So far, low-grade clay deposits have been ignored as potential candidates for cement industries. Therefore, a potential usage of multicomponent clay deposits (i.e., low-grade clay) as pozzolanic materials needs to be investigated.

Furthermore, addition of limestone to the cement-calcined clay mixture is an efficient known way to increase properties of the concrete due to the formation and stabilization of hemi-carboaluminate instead of monosulfoaluminate in the cement structure at early stages of hydration, which will be converted to monocarboaluminate after 90 days. It leads to an increase in the amount of free sulfate in the system and formation of ettringite that is an expansive phase. So, the total volume of the hydrate phase increases. On the other hand, the limestone-calcined clay mixture shows much stronger pozzolanic reactivity than the calcined clay alone. However, the efficiency and pozzolanic reactivity of the SCM obtained from the limestone-calcined clay mixture are still affected from the mineralogical purity of the used clay.

US 4737191 A discloses a process for the preparation of hydraulic binders by applying heat treatment on a raw material containing intimately mixed clay phases and calcium carbonate, at a temperature between 700 and 900 degrees C; applying, during the heat treatment of said material, a sufficient partial pressure of carbonic

gas to oppose the thermal dissociation of the calcium carbonate in excess of that which directly combines with the clay phases; whereby there is obtained simultaneously both activation of the clay phases by dehydroxylation (pozzolanic activation) and reaction of said dehydroxylated clay phases directly with a portion of the calcium carbonate to form lime combinations with potential hydraulic properties, without formation of free lime; and mixing the obtained active product with clinker, wherein the amount of active product in the mixture does not exceed 95%. US 4737191 A aims to prepare a SCM that especially prevents the formation of any free lime during the heating treatment.

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WO 2017202849 A1 proposes a method for producing a supplementary cementitious material comprising converting dolomite ($\text{CaMg}(\text{CO}_3)_2$) and aluminium silicate (containing Al_2O_3 and SiO_2) to supplementary cementitious material by burning them under reducing conditions in the temperature range of $>700^\circ\text{C}$ to 1100°C if no mineralisers are contained, and in the temperature range of 625°C to 950°C if mineralisers are contained. Furthermore, WO 2017202849 A1 illustrates experiments carried out on different types of clays by burning them with or without dolomite or limestone at different temperatures; and also shows comparative results of said experiments based on the compressive strengths of obtained SCMs. In conclusion, it notifies that an already high-grade clay material can be improved better than low-grade clay materials by burning.

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Accordingly, there is a need for providing a novel SCM produced by activation of a schist type material (low-grade clay) which is more available and cost effective than high-grade clay deposits and furthermore which has high efficiency and pozzolanic reactivity value as in known SCMs produced from activation of high-grade clay deposits.

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Objects of the Invention

Primary object of the present invention is to overcome the abovementioned shortcomings of the prior art.

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Another object of the present invention is to provide a supplementary cementitious material (SCM) and a method for producing the same with minimized carbon dioxide emission.

- 5 Another object of the present invention is to provide a highly reactive supplementary cementitious material (SCM) produced by activation of a low-grade clay and a method for producing the same.

- 10 Another object of the present invention is to provide a supplementary cementitious material (SCM) and a method for producing the same, where the activation of starting materials takes place at even lower temperatures.

- 15 Another object of the present invention is to provide a binder and also a concrete material obtained with even greater energy savings and with minimized carbon dioxide emission.

Another object of the present invention is to provide a binder and also a concrete material having improved mechanical and durability properties.

- 20 A further object of the present invention is to provide a binder and concrete material with a comparatively high content of supplementary cementitious material.

Summary of the Invention

- 25 The present invention proposes a supplementary cementitious material (SCM) comprising an activated mixture having at least an activated clay-based material and an activated calcium-based material, wherein said activated mixture is obtained by subjecting a mixture of at least a clay-based material and a calcium-based material together into an activation (instead of separate activation) treatment till 70-95 %, preferably until 70-90% of said calcium-based material is activated . Said mixture
30 comprises the clay-based material in an amount minimum 70% by weight of the mixture where said clay-based material contains clay source of at least 40% by

weight; and the calcium-based material in an amount between 10-30% by weight of the mixture where said calcium-based material contains calcium source of at least 50 % by weight.

- 5 According to an embodiment of the present invention, said clay-based material is a mixture having at least one or more of kaolinite, illite, smectite, zeolites and amorphous aluminosilicates. According to another embodiment, said calcium-based material is any calcium source that gives free-lime (CaO) upon thermal decomposition below 900 °C. Preferably, said calcium-based material comprises one
10 or more of any one of calcium carbonate phases, dolomitic carbonates with calcium content and calcium sulphates.

- According to an embodiment, the mixture of said clay-based material and said calcium-based material has been subjected to a thermal treatment or a mechanical
15 treatment for obtaining the activated mixture and producing the SCM according to the present invention. The thermal treatment is performed by heating the mixture of said clay-based material and said calcium-based material together up to a treatment temperature between 700-900°C. Optionally, said mixture has been heated to the treatment temperature by constant increment in temperature at a rate of 10 °C/min.
20 Optionally, the ratio of activated Ca ions to activated Si+Al ions lays between 1.5 to 3.0.

- The present invention further proposes a method for producing SCM comprising the steps of (a) providing a mixture of at least a clay-based material and a calcium-
25 based material; and (b) subjecting said mixture to an activation treatment for obtaining an activated mixture until 70-95 %; and preferably until 70-90 % of said calcium-based material is activated. Furthermore, amount of the clay-based material in said mixture is minimum 70 % by weight of said mixture, where said clay-based material contains clay source of at least 40 % by weight; and amount of
30 the calcium-based material in said mixture is between 10-30 % by weight of said mixture, where said calcium-based material contains calcium source of at least 50 % by weight.

According to an embodiment, in step (b) of the disclosed method, said mixture has been subjected to a mechanical treatment or a thermal treatment for obtaining said activated mixture. According to thermal treatment embodiment, the mixture of said clay-based material and said calcium-based material together is heated up to a treatment temperature between 700-900°C. Optionally, said mixture has been heated to the determined treatment temperature by constant increment in temperature at a rate of 10 °C/min. The method may optionally comprise a step for cooling the obtained activated mixture, performed after method step (b). Optionally, the mixture of the starting materials is isothermally kept at the treatment temperature for a predetermined duration.

Furthermore, the invention discloses a binder comprising a mixture of cement and SCM according to present invention; and also concrete material comprising such a binder.

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Brief Description of the Figures

The figures whose brief explanations are herewith provided are solely intended for providing a better understanding of the present invention and are as such not intended to define the scope of protection or the context in which said scope is interpreted in the absence of the present description.

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Fig. 1 presents TGA of L1, L2 and L3 samples

Fig. 2a presents DSC/TGA curve of L1 sample between 25-300 °C

Fig. 2b presents DSC/TGA curve of L1 sample between 300-1000 °C

25 Fig. 3a presents DSC/TGA curve of L2 sample between 25-300 °C

Fig. 3b presents DSC/TGA curve of L2 sample between 300-1000 °C

Fig. 4a presents DSC/TGA curve of L3 sample between 25-300 °C

Fig. 4b presents DSC/TGA curve of L3 sample between 300-1000 °C

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Detailed Description of the Invention

The present invention concerns a novel supplementary cementitious material (SCM); a method for producing the same and a binder containing a mixture of said novel SCM with cement, optionally with ordinary Portland cement (OPC).

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Supplementary cementitious materials (SCMs) disclosed according to the present invention are materials that contribute to the properties of cement through hydraulic or pozzolanic reactions where pozzolanic reaction is characterized by the consumption of calcium hydroxide (CH) by reactive silica or alumina contained in
10 pozzolans, forming calcium-silicate hydrate (C-H-S) or calcium aluminium silicate hydrate (C-A-S-H). SCMs are generally used to partially replace the Portland cement component, and the level of replacement varies from around 10 % to 50 % depending on the nature (especially mineralogical and chemical composition) of the replaced SCM. Generally, the required amount of SCM decreases as the reactive
15 silica content of the SCM increases or as the calcium or alkali content of the SCM decreases.

The novel supplementary cementitious material according to the present invention comprises an activated mixture having at least an activated clay-based material and
20 an activated calcium-based material, where said activated mixture of the activated clay-based material and the activated calcium-based material is obtained by subjecting a mixture of at least a clay-based material and a calcium-based material together into an activation treatment till 70-95 % by weight of said calcium-based material is activated. Furthermore, the amount of the materials in starting mixture
25 (the mixture of at least a clay-based material and a calcium-based material) is well regulated. Accordingly, the amount of said clay-based material(s) is minimum 70 % by weight of the mixture, and the amount of said calcium-based material(s) is between 10-30 % by weight of the mixture, i.e. the mixture of the clay-based material(s) and the calcium-based material(s) before activation treatment is
30 performed. Additionally, the clay-based material of the mixture contains clay source at least 40% by weight said clay-based material; and the calcium-based material contains calcium source at least 50 % by weight of said calcium-based material.

As used herein, the term "clay-based material" refers to a solid material comprising a mixture of several clay minerals (such as kaolinite, smectite, illite and montmorillonite) generally associated with non-clay minerals, which are strongly affected by the nature of the parent rocks. Thereby, clay-based materials according to the present invention are also named as schist type materials instead of pure clayey phases. Clay-based materials generally comprise a mixture of aluminosilicates, quartz, carbonates, and/or other minor phases. They are almost well distributed geographically on the earth and have pozzolanic characteristics after being activated by a treatment process. The amount of the clay source (pure clayey phases) in a clay-based material according to the present invention is at least 40% by weight, and preferably exceeds 50% by weight of total phase distribution, where the remaining shall be understood as the amount of non-clay minerals, i.e. impurities. In other words, the clay-based material of the mixture contains clay source (pure clayey phases) in an amount between 40% and 100%. The increase in the amount/percentage of the clay source in said clay-based material improves the advantageous effects of the SCM according to the present invention. Furthermore, the clay based material of the present invention shall be understood as a resource for Si ions and optionally Al ions. According to an embodiment of the present invention, said clay-based material is a mixture having at least one or more of kaolinite, illite, smectite, zeolites and any amorphous aluminosilicates.

The term "calcium-based material" disclosed herewith shall be understood as source of calcium ions. Preferably the calcium-based material according to the present invention may be any calcium source that gives CaO upon thermal decomposition below 900 C. Optionally, said calcium-based material comprises one or more of any one of calcium carbonate phases, dolomitic carbonates with calcium content and calcium sulphates.

The skilled person will understand that a given "clay-based material", a given "calcium-based material" or a given "mixture of at least a clay-based material and at least a calcium-based material" ("mixture" or "mixture of starting materials") have different properties before and after they have subjected to an activation treatment. Thus, an "activated clay-based material" has different properties as compared to the

original "clay-based material" prior to its activation treatment and an "activated calcium-based material" has different properties as compared to the original "calcium-based material" prior to its activation treatment. The same also applies to "mixture" and "activated mixture having at least an activated clay-based material and an activated calcium-based material" ("activated mixture").

The present invention basically relates to a novel SCM comprising an activated clay-based material and an activated calcium-based material and also to a proper activation method for rendering an effective SCM. The surprising and game-changing effect is obtained where activation treatment of said starting materials is performed together, i.e. the mixture of clay-based material and calcium-based material is subjected to activation treatment at the same time and same medium. Furthermore, the activation treatment of said mixture is terminated when 70-95 % (by weight) of said calcium-based material is activated. Activation percentage of calcium-based material may be measured by thermogravimetric (TGA) analysis, differential thermal analysis (DTA) or XRD analysis. The inventors of the present invention notified that activation of calcium-based material provides excessive source of Calcium ion (Ca^{2+}) as free-lime (CaO) and in case of the activation treatment is applied to a mixture of calcium-based material together with the activated clay-based material till 70-95 % of said calcium-based material is activated, the excessive source of Calcium ion (Ca^{2+}) as free-lime (CaO) provides strongly basic condition for forming more C-S-H (calcium-silicate hydrate) and C-A-S-H (calcium aluminium silicate hydrate) during the consequent hydration reactions upon being exposed to water. Moreover, the further reaction will prepare the hydroxyl ions that could attack the Si-O-Si or Si-O-Al bonding of complex clays and de-stabilize them to be reactive. As known, C-S-H and optionally the C-A-S-H are the main products of the hydration of Portland cement and this phase transformation and formation of strength developer products causes more durability of composite cement.

According to known thermogravimetry measurement techniques, the activation amount of materials is determined based on total amount of weight loss of said materials. However, the weight loss amount measured in said techniques may also include evaporation of absorbed water below 300 °C, where said evaporated water

is mainly not present in the structure of the material. Thereby, according to a preferred embodiment of the present invention, the amount of 70-95 % activation of the calcium-based material of the starting mixture corresponds to 75-95% of the total weight loss observed in the before-mentioned materials starting from the temperature of 300 °C. The same activation percentages can also be monitored with the help of XRD measurements by calculating the amount of crystalline calcium-based materials. The thermal activation process should continue until the 70-95 % of the crystalline calcium-based material(s) is decomposed.

According to a preferred embodiment of the present invention, the amount of the materials in the starting mixture is well regulated. Thus, the amount of said clay-based material(s) is minimum 70 % and the amount of said calcium-based material(s) is between 10-30 % by weight of the mixture, where the clay-based material of the mixture contains clay source at least 40% by weight said clay-based material; and the calcium-based material contains calcium source at least 50 % by weight of said calcium-based material. According to a preferred embodiment of the present invention, the amount of the clay source in a clay-based material is at least 50 % by weight of said clay-based material. The advantageous effect of the present invention on the produced SCMs is improved with the increasing percentage of the clay source in the clay-based material and also with the increasing percentage of the calcium source in the calcium-based material. In a preferred embodiment, the amount of calcium-based material is between 15-30% and more preferably 20-30% by weight of the starting mixture. Furthermore, the SCM disclosed according to the present invention comprises the activated mixture of clay-based material and calcium-based material –and thus sources thereof- where ratio of activated Ca ions to activated Si+Al ions lays between 1.5 to 3.0.

Different techniques such as mechanical treatment, chemical treatment or thermal treatment may be applied on the mixture of the starting materials to activate them and thus to obtain the activated mixture suitable for using as a SCM. According to the present invention, the activation of the mixture is preferably performed by using mechanical treatment or thermal treatment techniques. The mechanical treatment technique is mainly based on intensive grinding process where the effect of grinding

is two fold: first intensive grinding activates the mixture of clay based materials and calcium-based materials by interrupting their crystalline structure thereby making them vulnerable to basic aqueous solutions' attack; secondly grinding increases the surface area of the powders by increasing fineness of the ground mixture, which is optionally measured according to the Blaine surface area (cm^2/g) parameter. The inventors have already noted that in case of the mechanical treatment is sufficiently prolonged, an upper limit of activation can be reached and once the mixture of clay based and calcium-based materials are all amorphousized, there is no further advantages that can be gained in terms of pozzalanicity. Too fine of SCM powders influence also the workability of the binder negatively. On the other hand, the thermal treatment technique relates to application of heat to the mixture of the starting materials, where the maximum temperature applied on said mixture during the treatment is important. It is reported that the average activation temperature of multicomponent clay deposits (e.g. clay-based materials) is between 300 to 750 °C; and the average activation temperature of carbonates (e.g. calcium-based materials) is between 750 to 850 °C. In terms of the physical properties of the mixtures, it is known and accepted that the activation temperature (i.e. the maximum temperature applied to achieve activation) of a mixture depends on the amount of the materials constituting said mixture and their activation temperature. However, the inventors of the present invention noted that the average activation temperature of the mixture according to the present invention is between 700 to 900 °C according to thermogravimetric analysis. The determined temperature range is surprisingly different than expected, which is due to the interaction of the clay-based material with calcium-based material in the mixture during the activation process. The activation of clay-based schist type materials causes dehydroxylation of the clayey phases by reactivating them and also decomposes the calcium-based material. According to a preferred embodiment of the present invention, said mixture of starting materials has been subjected to thermal treatment by heating the mixture up to a treatment temperature between 750 to 900 °C, and more preferably around 850 °C. The thermal treatment applied to the mixture of starting materials is preferably carried out in a furnace or a reactor; where the temperature of the furnace or reactor in which said mixture is kept is raised from room temperature to the determined treatment temperature. Preferably, said mixture of the starting

materials is heated to the treatment temperature by constant increment in temperature at a rate of 10 °C/min.

If not otherwise specified any characterization as "approximately", "around" and similar expression in relation to a numerical value means that up to 10 % higher and lower values are included, preferably up to 5 % higher and lower values, and in any case at least up to 1 % higher and lower values, the exact value being the most preferred value or limit.

- 10 Co-activation of the starting materials (i.e. the mixture) and the activation ratio (70-95 %) of the calcium-based material are vital criteria for the present invention. The activation ratio refers the weight ratio of the amount of activated calcium-based material of the activated mixture to the amount of calcium-based material (before being subjected to activation treatment) of the starting mixture. According to a preferred embodiment of the present invention, the activation ratio of the calcium-based material is 70-90 %, more preferably 80-90 %, and most preferably around 80 %. The inventors of the present invention reported that, according to the thermogravimetric (TGA) analysis of any powder, the magnitude of activation treatment (i.e. applied heat or achieved fineness) corresponds to an amount
- 15 corresponding to 70-95%, preferably to 70-90 %, more preferably 80-90 %, and most preferably around 80 % of the total weight loss. The given percentages cause avoiding dead-burning of the clay-based material; and reactivate the materials of the mixture to the proper stage.
- 20
- 25 The term "dead-burning" here means overheating of the material which causes said material to lose a substantial amount of its pozzolanic reactivity (in other words its binding capacity).

- The term "activation" means changing one or more of chemical properties, crystallinity, phase composition, three dimensional array and binding behaviour of the structural atoms induced by applying energy. According to an embodiment of the present invention, the term activation/activated means dehydroxylation of/ dehydroxylated clay-based material; or calcination of/ calcined calcium-based material. Dehydroxylation involves optionally the heating process through which the
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hydroxyl group (OH) is released by forming a water molecule and results in the loss of structural water, and the destruction of the crystal structure of the clayey material. Calcination is used to mean a thermal treatment process to bring about a thermal decomposition. Decomposition temperature of a substance is the
5 temperature at which the substance chemically decomposes. The reaction is usually endothermic as heat is required to break chemical bonds in the compound undergoing decomposition.

A method for producing a supplementary cementitious material according to the
10 present invention comprises the method steps of (a) providing a mixture of at least a clay-based material and a calcium-based material; and (b) subjecting said mixture to an activation treatment for obtaining an activated mixture until 70-95% of said calcium-based material is activated.

15 In the step (a), the mixture of the starting materials preferably comprises said calcium-based material in an amount between 10-30% by weight of the mixture; and said clay-based material in an amount of minimum 70% by weight of the mixture. Furthermore, said clay-based material contains clay source of at least 40% by weight; and said calcium-based material contains calcium source of at least 50 %
20 by weight.

According to another embodiment, said mixture of the starting materials has been subjected to activation treatment together until 70-90% of said calcium-based material is activated, more preferably until 80-90, and most preferably until around
25 80 % of said calcium-based material is activated.

Disclosed activation of the mixture of starting material is optionally performed by applying thermal treatment or mechanical treatment on said mixture. The mechanical treatment technique is mainly based on a grinding step.

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In case of thermal treatment is applied to the mixture of the starting materials, said mixture has been subjected to a thermal treatment, by heating the mixture up to a temperature between 700 to 900°C, preferably between 750 to 900 °C, and more preferably around 850 °C. Optionally, said mixture has been heated to determined

temperature by constant increment in temperature at a rate of 10 °C/min. Accordingly, the temperature will increase up the start point of decomposition and will wait isothermally for a term until 70-95% (preferably 70-90%, more preferably 80-90% and most preferably around 80 %) of said calcium-based material is decomposed. In step (b) of above disclosed method, the duration for keeping the mixture of starting materials isothermally at the determined treatment temperature for decomposing (activating) the same can be determined based on the amount of starting mixture and amount of the impurities therein. Furthermore, range of the treatment duration may be determined according to thermogravimetric analysis. This isothermal heat scenario causes the heat to be distributed uniformly through the mixture and homogeneity of activation. Furthermore, in a case where the decomposition is continued for a duration shorter than a predetermined treatment duration, the desired activation percentage of the calcium-based material could not be reached and in a case where the decomposition is continued for a duration longer than a predetermined treatment duration, dead-burning of the mixture of starting materials occurs.

The inventors of the present invention measured that required amount of heat for activating the starting mixture according to claim 12 or claim 13, is approximately 0.3 kJ per gram of clay-based material which decomposes between 350 and 700 °C, and approximately 0.5 - 0.6 kJ per gram of calcium-based material which decomposes between 650 and 900 °C.

The method of the present invention may optionally comprise step (c) where the obtained activated mixture after step (b), i.e. the produced SCM, is typically cooled down to room temperature. The mixture can also be cooled rapidly i.e., for preventing phase transformation or crystallization. Optionally, the cooling treatment is performed by air quenching which will ascertain the decomposition and consequently reactivation of materials. It is better to air quench the heat-treated and activated mixture on the metallic plate which has the proper thermal conductivity.

Furthermore, a novel binder is obtained by providing a mixture of cement and the supplementary cementitious material according to the present invention.

Accordingly, the binder of the present invention comprises cement and SCM which comprises activated mixture of at least an activated clay-based material and an activated calcium-based material, wherein the clay-based material has been activated together with the calcium-based material till 70-95 % of said calcium-based material is activated. The binder of the present invention preferably contains up to %45, more preferably 20 to 40 % and even more preferably around 30% SCM by weight. The cement disclosed herewith is optionally ordinary Portland cement (OPC). In addition, the present invention proposes a concrete material comprising the binder of the present invention, together with optional admixtures and aggregates. Optionally, said concrete material is prepared with a water/cement ratio of 0.5.

Examples:

Samples of starting mixtures (L1, L2 and L3) are prepared, which respectively contain 0%, 9% and 15% of calcium carbonate, where sample L3 is a mixture according to the present invention. In order to determine the proper temperature for activation that should be applied to each sample, TGA (NETZSCH STA 449 JUPITER, Selb, Germany) analyses were performed. Figure 1 represents a comparison of the thermo-gravimetric analysis (TGA) graphs among the samples. Based on the TGA results, the activation temperatures of the samples were determined as provided in below given Table 1.

Table 1. Calcination temperatures of L₁, L₂ and L₃ samples

Sample	Calcination Temperature
L ₁	600 °C
L ₂	750 °C
L ₃	800 °C

With the help of DSC (Mettler Toledo TGA/DSC) analysis, the exact energy amount needed for each sample to be activated is determined. It is noted that the energy amount of samples differs based on the portions of calcium carbonate and clay in the mixture. Figures 2, 3 and 4 illustrate the DSC/TGA curves of the L₁, L₂ and L₃ samples, respectively. Additionally, for each weight loss step, the areas under the curve were integrated which is equivalent to the energy consumption.

After activation treatment, it was noted that since the sample materials are all a type of very good thermal insulator, the duration of activation of a sample in different amounts such as 50 mg and 600 g are not the same. As it can be seen in figures 2-4, the area under the peak related to each step of decomposition was calculated for each sample. These integrated values are equivalent to the energy which has been consumed during the decomposition. By dividing the energy value of one step by the weight loss of the same step, the enthalpy (ΔH -KJ/gr) value could be calculated. Table 2 represents the ΔH values of the samples.

Table 2. Enthalpy (ΔH) values of the L₁, L₂ and L₃ samples

Sample	Decomposition Enthalpy (KJ/gr)	Total (KJ/gr)
L ₁	ΔH_1 0.44	0.71
	ΔH_2 0.27	
	ΔH_3 0	
L ₂	ΔH_1 2.22	2.92
	ΔH_2 0.25	
	ΔH_3 0.45	
L ₃	ΔH_1 2.37	3.4
	ΔH_2 0.34	
	ΔH_3 0.69	

Referring to the Table 2 given above, it was concluded that energy amount (KJ) per weight (gr) of the samples that is required for activating any sample according to the present invention increases by increasing the amount of the calcium carbonate (i.e. calcium source) in the sample. It further means that with respect to the calcium

5 source amount of the sample, the activation temperature and the total given energy should be changed as well. Owing to the fact that decomposition of the clay-based material starts and ends earlier than decomposition of the calcium-based material, if excessive energy for calcium-based material decomposition is spent and if the decomposition of calcium phase (calcium-based material) is driven to the end, it will

10 make dead-burned clay-based material. Therefore, any dead-burnt sample does not contain any active clayey material for being used in cement pozzolanic reactions. For schist type of materials (i.e., the mixture according to the present invention) it must be made sure that all the calcium carbonate is not decomposed for avoiding overheating which causes dead-burning of clay-based material. For the activation of

15 calcium-based material in a mixture as claimed, a good amount is 70-95% of the total calcium based material amount for obtaining improved advantage of the present invention.

Reference to "an embodiment" throughout this specification means that a particular

20 feature, structure or characteristic described in connection with the embodiment is included in at least one embodiment of the present invention. Thus, throughout this specification, the phrases "in one embodiment" or "in an embodiment" may not necessarily all referring to the same embodiment, but also may. Additionally, the particular features, structures or characteristics may be combined in any suitable

25 manner, as would be apparent to a person skilled in the art from this disclosure, in one or more embodiments. Furthermore, while some embodiments described herein include some but not other features included in other embodiments, combinations of features of different embodiments are meant to be within the scope of the invention, and form different embodiments, as would be understood by those in the art. For

30 example, in the following claims, any of the claimed embodiments can be used in any combination.

Claims:

1. A supplementary cementitious material comprising an activated mixture having at least an activated clay-based material and an activated calcium-based material,
5 wherein said activated mixture is obtained by subjecting a mixture of at least a clay-based material and a calcium-based material together into an activation treatment till 70-95 % of said calcium-based material is activated; and
- amount of the clay-based material in said mixture is minimum 70% by weight of said mixture, where said clay-based material contains clay source of at least 40% by
10 weight;
-amount of the calcium-based material in said mixture is between 10-30% by weight of said mixture, where said calcium-based material contains calcium source of at least 50 % by weight.
- 15 2. A supplementary cementitious material according to claim 1 wherein said clay-based material is a mixture comprising at least one or more of kaolinite, illite, smectite, zeolites and amorphous aluminosilicates.
3. A supplementary cementitious material according to claim 1 or 2 wherein said
20 calcium-based material is any calcium source that gives free-lime (CaO) upon thermal decomposition below 900 °C.
4. A supplementary cementitious material according to claim 3, wherein said calcium-based material comprises one or more of any one of calcium carbonate
25 phases, dolomitic carbonates with calcium content and calcium sulphates.
5. A supplementary cementitious material according to any one of the previous claims wherein said mixture of the clay-based material and the calcium-based material has been subjected to activation treatment together, until 70-90% of said
30 calcium-based material is activated.
6. A supplementary cementitious material according to any one of the previous claims wherein said mixture has been subjected to a thermal treatment, by heating the mixture up to a treatment temperature between 700-900°C.

7. A supplementary cementitious material according to claim 6 wherein said mixture has been heated to the treatment temperature by constant increment in temperature at a rate of 10 °C/min.

5

8. A supplementary cementitious material according to any one of the claims 1 to 5 wherein said mixture has been subjected to mechanical treatment for obtaining said activated mixture.

10 9. A supplementary cementitious material according to any one of the previous claims wherein ratio of activated Ca ions to activated Si+Al ions lays between 1.5 to 3.0.

15 10. A method for producing a supplementary cementitious material comprising the steps of:

a) providing a mixture of at least a clay-based material and a calcium-based material; wherein

20 - amount of the clay-based material in said mixture is minimum 70% by weight of said mixture, where said clay-based material contains clay source of at least 40% by weight;

-amount of the calcium-based material in said mixture is between 10-30% by weight of said mixture, where said calcium-based material contains calcium source of at least 50 % by weight.

25 b) subjecting said mixture to an activation treatment for obtaining an activated mixture until 70-95% of said calcium-based material of the mixture is activated.

11. A method for producing a supplementary cementitious material according to claim 10, wherein said mixture of the clay-based material and the calcium-based material has been subjected to activation treatment together, until 70-90 % of said
30 calcium-based material is activated.

12. A method for producing a supplementary cementitious material according to claim 10 - 11, wherein said mixture has been subjected to a thermal treatment, by heating the mixture up to a treatment temperature between 700-900°C.

13. A method for producing a supplementary cementitious material according to claim 12, wherein said mixture has been heated to determined treatment temperature by constant increment at a rate of 10 °C/min.

5

14. A method for producing a supplementary cementitious material according to claim 10 or 11 wherein said mixture has been subjected to a mechanical treatment for obtaining said activated mixture.

10 15. A method for producing a supplementary cementitious material according to any one of the claims 9 to 14 wherein ratio of activated Ca ions to activated Si+Al ions lays between 1.5 to 3.0.

15 16. A method for producing a supplementary cementitious material according to any one of the claims 10 to 15, wherein the method further comprises the step of:
(c) cooling down the obtained activated mixture after step (b).

17. A method for producing a supplementary cementitious material according to claim 12 or 13, in step (b), the mixture of the starting materials is isothermally kept
20 at the treatment temperature for a predetermined duration.

18. A binder comprising a mixture of cement and the supplementary cementitious material according to any one of the claims 1-9.

25 19. Concrete material comprising the binder according to claim 18.

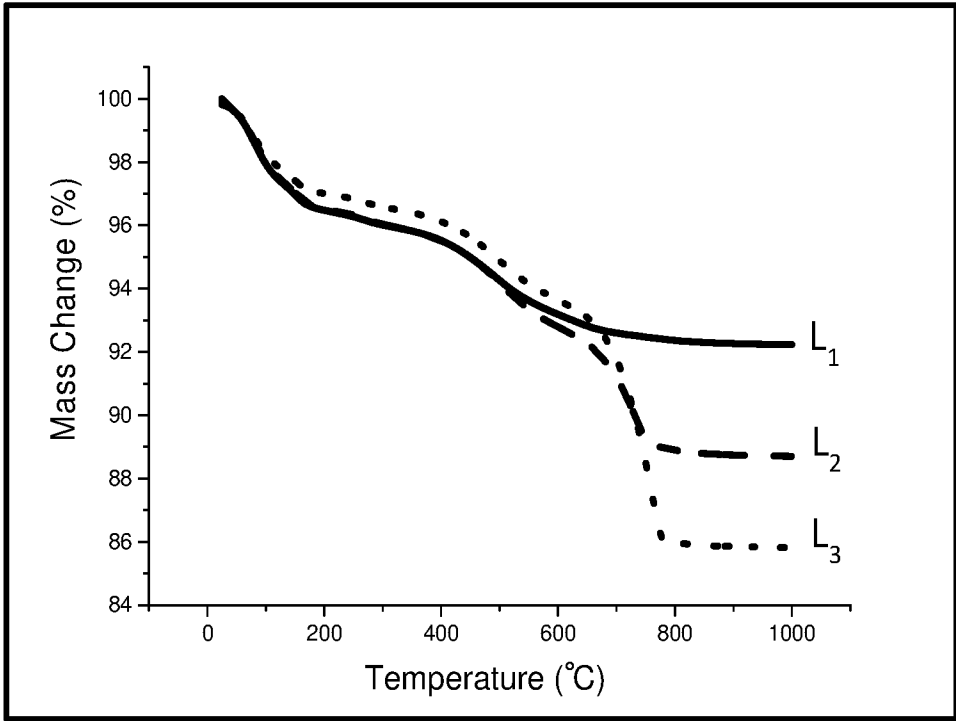
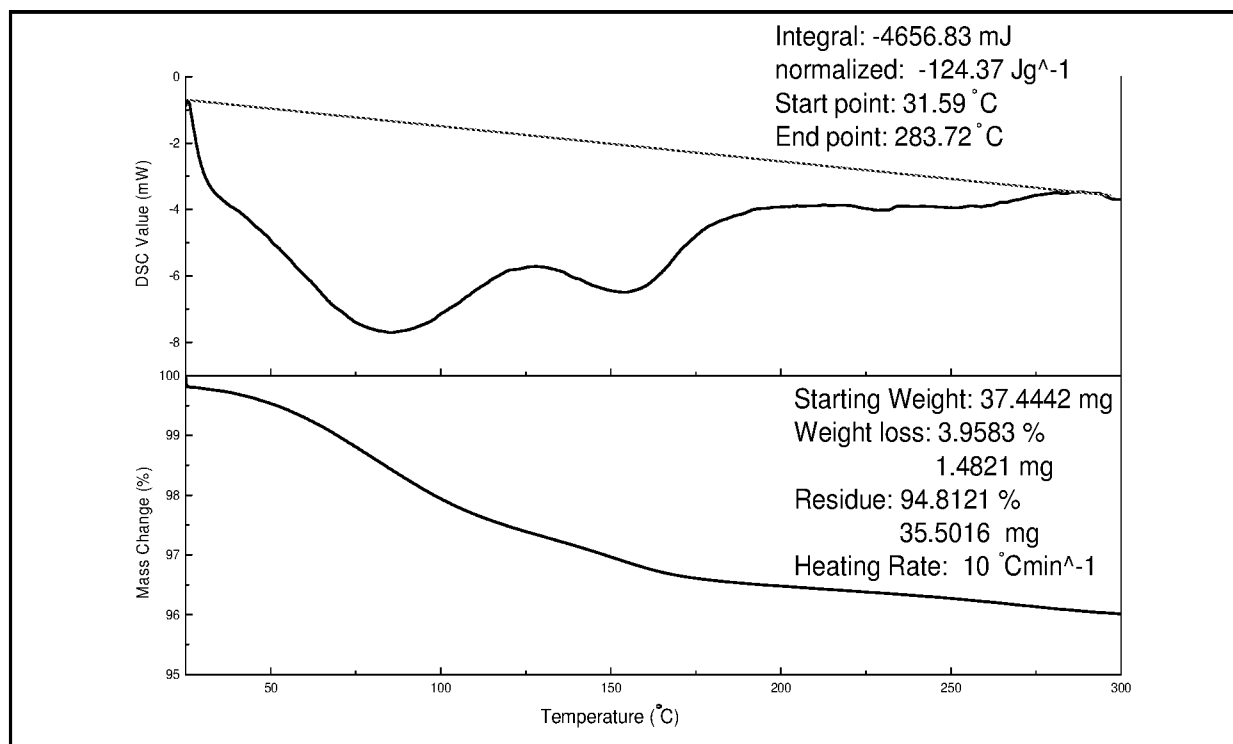
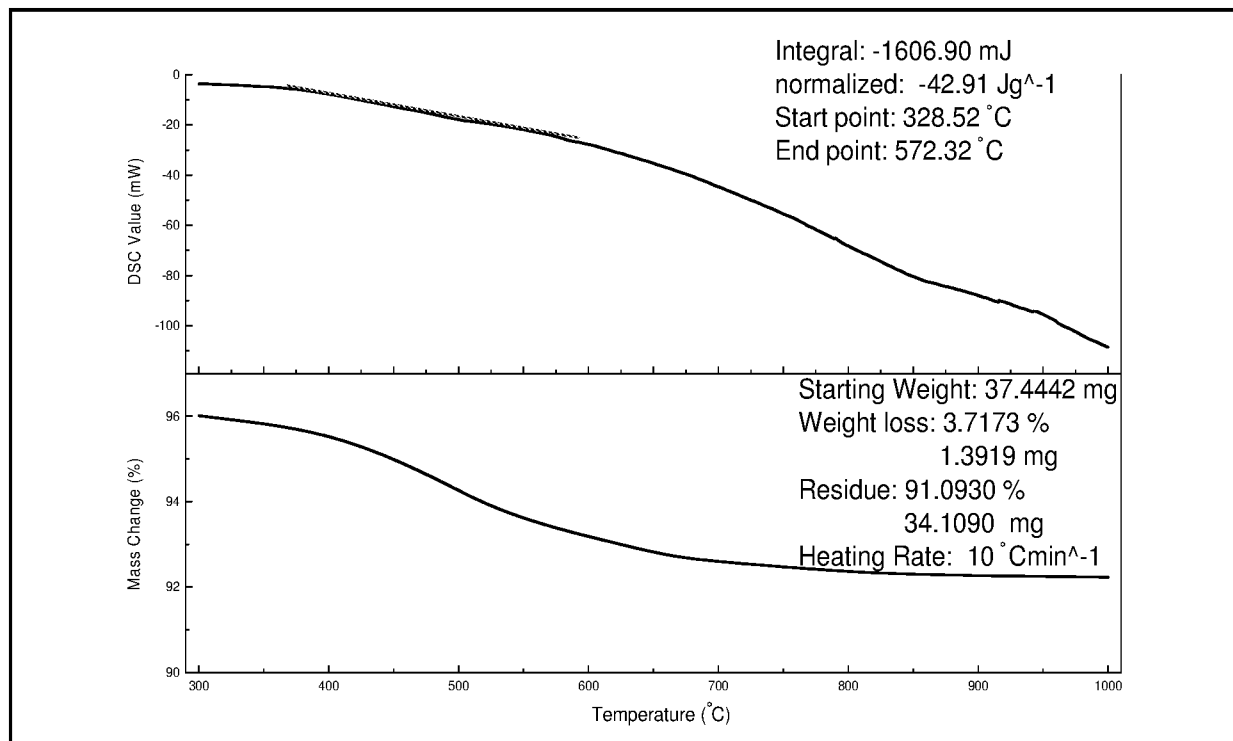


FIG.1

**FIG.2a****FIG.2b**

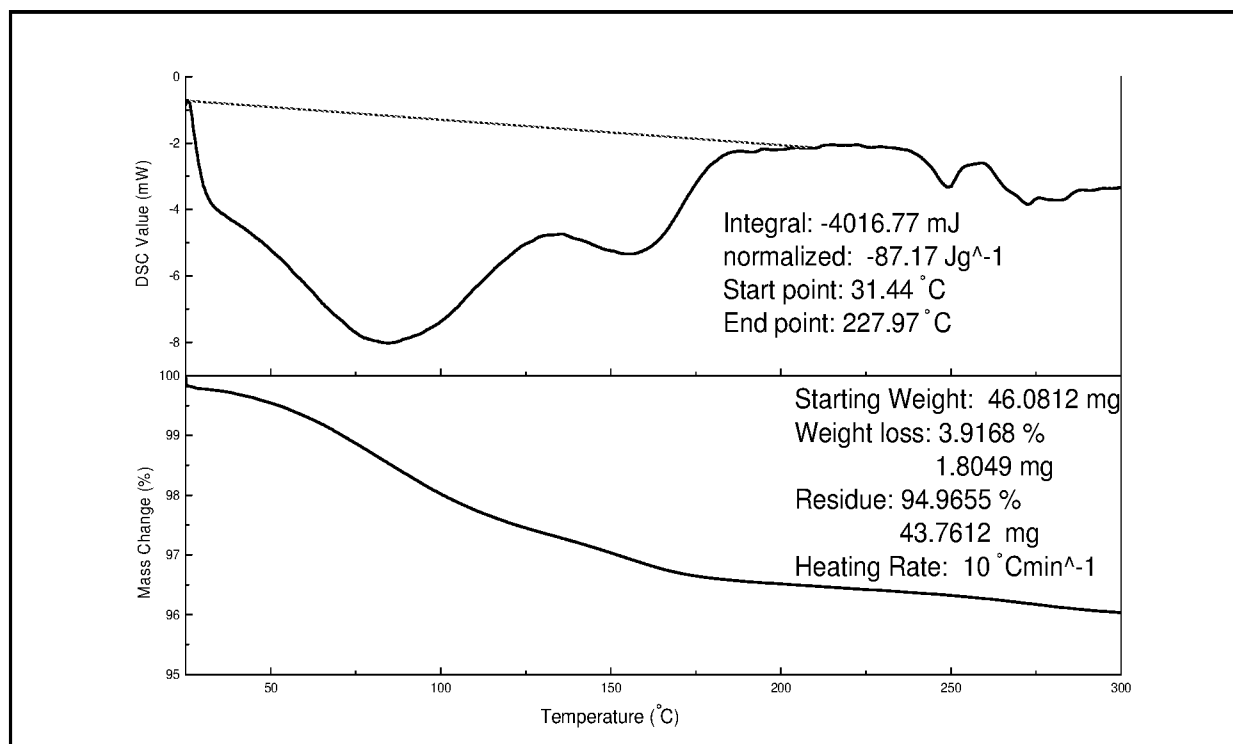


FIG.3a

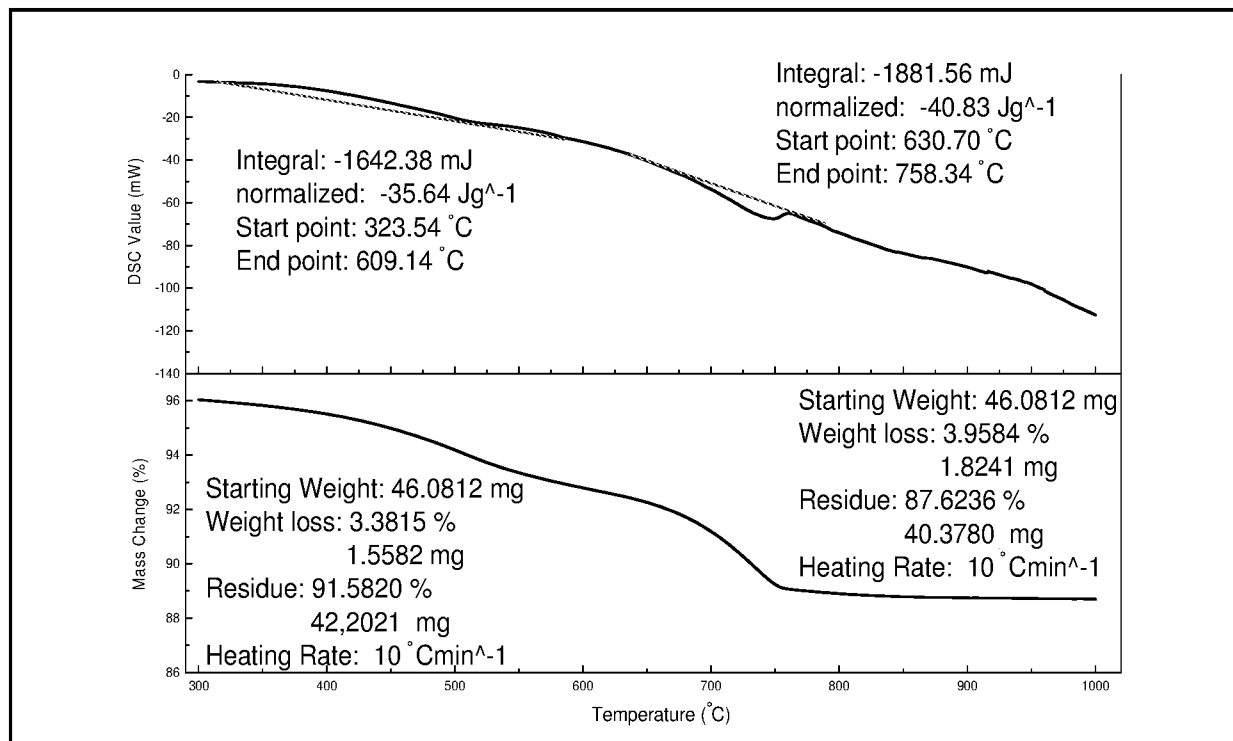
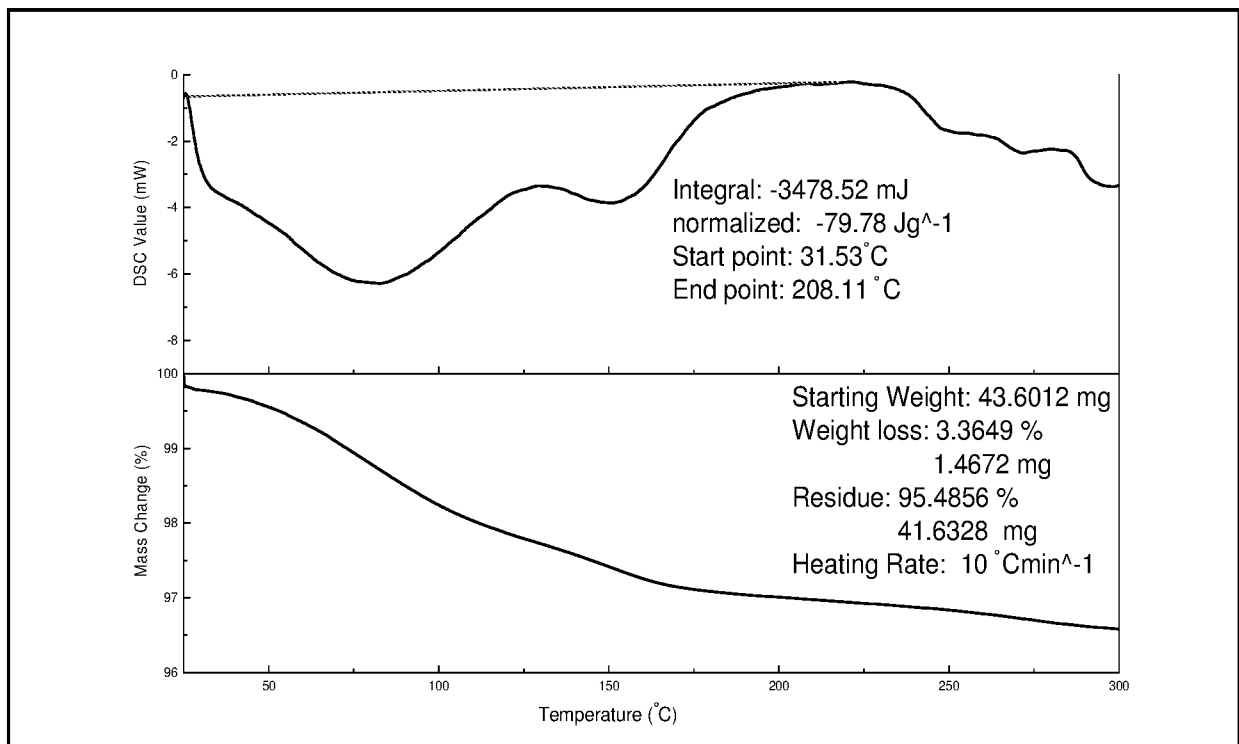
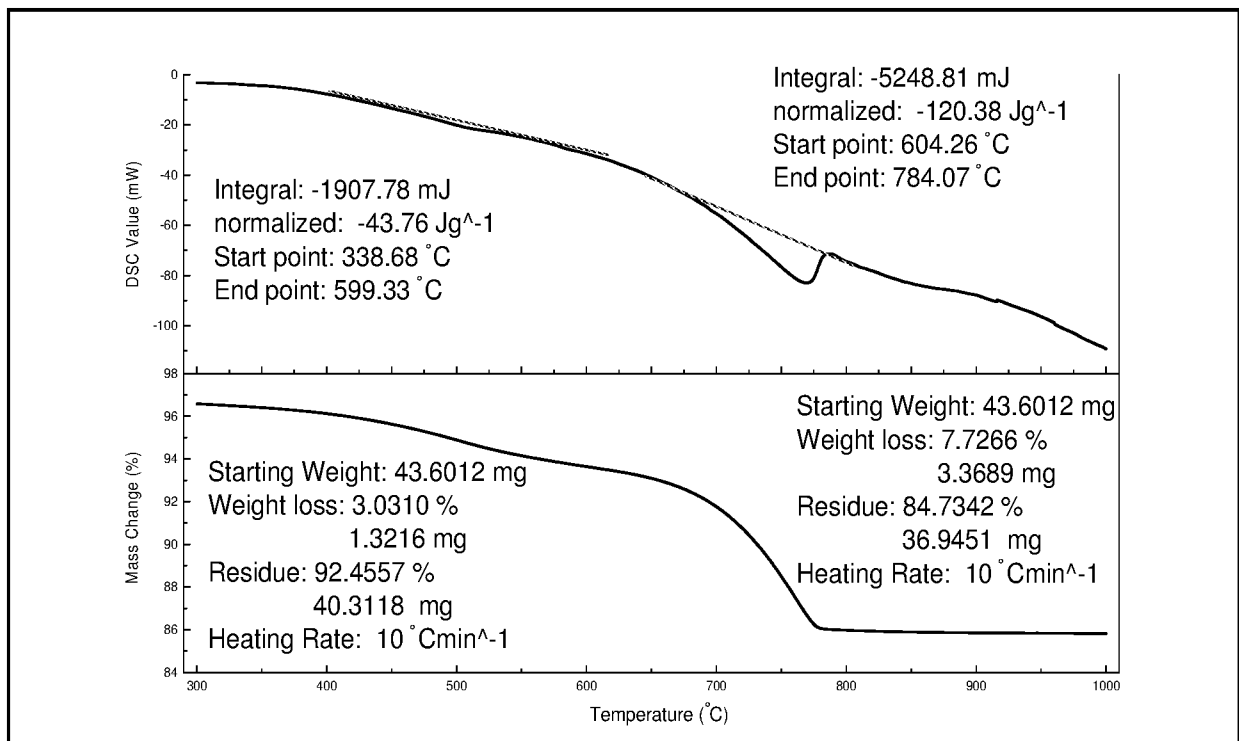


FIG.3b

**FIG.4a****FIG.4b**

INTERNATIONAL SEARCH REPORT

International application No
PCT/TR2020/050597

A. CLASSIFICATION OF SUBJECT MATTER
INV. C04B7/13
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2017/202849 A1 (HEIDELBERGCEMENT AG [DE]) 30 November 2017 (2017-11-30) the whole document -----	1-19



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

22 March 2021

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Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Roesky, Rainer

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/TR2020/050597

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2017202849 A1	30-11-2017	CA 3025054 A1	30-11-2017
		EP 3248952 A1	29-11-2017
		EP 3464211 A1	10-04-2019
		PL 3464211 T3	30-11-2020
		US 2019144339 A1	16-05-2019
		WO 2017202849 A1	30-11-2017
