(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) **World Intellectual Property Organization**
International Bureau

(43) **International Publication Date**
06 March 2025 (06.03.2025)

(10) **International Publication Number**
WO 2025/046104 A1

(51) **International Patent Classification:**
C21C 1/02 (2006.01) *C21C 7/076* (2006.01)
C21C 7/00 (2006.01) *C22B 1/244* (2006.01)
C21C 7/06 (2006.01) *C22B 7/02* (2006.01)
C21C 7/064 (2006.01)

(21) **International Application Number:** PCT/EP2024/074346

(22) **International Filing Date:** 30 August 2024 (30.08.2024)

(25) **Filing Language:** English

(26) **Publication Language:** English

(30) **Priority Data:**
23306460.9 01 September 2023 (01.09.2023) EP

(71) **Applicant: S.A. LHOIST RECHERCHE ET DEVELOPPEMENT** [BE/BE]; rue Charles Dubois 28, 1342 Ottignies-Louvain-la-Neuve (BE).

(72) **Inventor: PERRIN, Eric**; 7, boulevard des Martyrs Nantais de la Résistance, 44200 Nantes (FR).

(74) **Agent: GEVERS PATENTS**; De Kleetlaan 7A, 1831 Diegem (BE).

(81) **Designated States** *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CV, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IQ, IR, IS, IT, JM, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, MG, MK, MN, MU, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) **Designated States** *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, CV, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SC, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, ME, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report (Art. 21(3))*
— *in black and white; the international application as filed contained color or greyscale and is available for download from PATENTSCOPE*

(54) Title: COMPOSITION FOR USE IN A STEEL MAKING PROCESS

(57) **Abstract:** The present invention relates to a composition for use in a steel making process [composition (C), herein after], wherein said composition (C) is prepared by mixing (i) at least one steel scale by-product [compound (SSB), herein after] which comprises equal to or more than 35.0 wt. % of free water, relative to the total weight of the compound (SSB) and (ii) at least one first additive in an amount providing a weight ratio of calcium oxide to the free water present in the compound (SSB) equal to or more than 1.50, wherein said first additive comprises calcium oxide in an amount of at least 80.0 wt. %, relative to the total weight of the first additive. The composition (C) after mixing comprises free water in an amount equal to or less than 5.0 wt. %, relative to the total weight of the composition (C).

“Composition for use in a steel making process”

Field of invention

The present invention relates to a composition for use in steel making process. The present invention further relates to the method for production of the composition, to the use of the composition as raw material in steel making process and to a premix for producing the composition.

Background of the invention

During the steelmaking process, wastes, also called by-products, such as slag, dust, and sludge are generated, which contain hazardous chemicals and metals. If not handled correctly, these wastes can contaminate the environment, harm human health, and damage ecosystems. These wastes are currently mostly disposed of to landfill. However, disposal of large volumes of metallic solid waste may disturb the environmental balance of soil and groundwater.

Recycling is becoming very important. Recycling is a process using materials (waste) into new products to prevent waste of potentially useful materials, reduce the consumption of fresh raw materials, reduce energy usage, reduce air pollution (from incineration) and water pollution (from landfilling) by reducing the need for "conventional" waste disposal. Recycling is a key component of modern waste reduction. The European Union is also currently updating its legislation on waste management to promote a shift to a more sustainable model known as the circular economy.

Therefore, it is known to recycle and reuse for example, BOF and LAF slag’s into cement, concrete and road base infrastructure markets, leading to significant reductions in environmental impact, along with high-efficiency metal recovery and the manufacture of co products from the residual slag’s.

For example, the document of Maschio et al. describes the use of steel scale waste as component in mortars production (“*Steel scale waste as component in mortars production: An experimental study”,* Case Studies in Construction Materials 4 (2016) 93–101). In this document, steel scale waste which is a by-product of steel production, replaces part of the fine fraction of the natural aggregate used in a mixture with cement to produce mortars.

It is also known from the document of Goi *et al.* to use steel scale waste as a heterogeneous catalyst for the treatment of liquid waste because it is a rich iron source. ("*Steel Scale Waste as a Heterogeneous Fenton-like Catalyst for the Treatment of Landfill Leachate*", Ind. Eng. Chem. Res. 2021, 60, 31, 11715–11724).

Notably, EP0687309 A1 also discloses a process and a device for recovering iron and carbon from blast furnace scrubber sludge (dust, particulates and sludge). After a series of treatments such as separations by filtration or hydro cyclones, the recovered iron and carbon are recycled to the iron making operation

The steel making industry is also affected by the concerns of recycling and circular economy and is currently undergoing an energy transition. It must notably adapt its dependence on raw materials in line with constantly changing regulations.

However, in view of the specific requirements of the steel making industry, use of recycled products in this field is very challenging. For this reason, at the moment, a lot of wastes or by-products from steel making process cannot be reused in a steel making process. This is also the reasons why most of the literature concerning the recycling and the reuse of steel making wastes is in the field of construction (cement, mortars…) where it is easier to use raw materials derived from waste without dramatically impacting the qualities of the end product.

In view of the above, there is a strong need for an improved composition for use in steelmaking process, which allows a by-product from steel making process to be recycled and reused as raw material in a steelmaking process.

Summary of the invention

The inventors have now surprisingly found that it is possible to provide a composition fulfilling the above mentioned needs.

Thus, there is now provided a composition for use in a steel making process [composition (C), herein after], wherein said composition (C) is prepared by mixing :

(i) at least one steel scale by-product [compound (SSB), herein after] which comprises equal to or more than 35.0 wt. % of free water, relative to the total weight of the compound (SSB);

(ii) at least one first additive in an amount providing a weight ratio of calcium oxide to the free water present in the compound (SSB) equal to or more than 1.50, wherein said first additive comprises calcium oxide in an amount of at least 80.0 wt. %, relative to the total weight of the first additive, and

characterised in that the composition (C) after mixing comprises free water in an amount equal to or less than 5.0 wt. %, relative to the total weight of the composition (C).

In another aspect the present invention further provides a method for the manufacturing of a composition for a use in steel making process, as detailed above, a premix for manufacturing the composition, as detailed above and use of the composition as raw material in a steel making process, as detailed above.

Detailed description

As used herein and in the claims, the terms “comprising” and “including” are inclusive or open-ended and do not exclude additional unrecited elements, compositional components, or method steps. Accordingly, the terms “comprising” and “including” encompass the more restrictive terms “consisting essentially of” and “consisting of”.

The term “comprising”, used in the claims, should not be interpreted as being restricted to the means listed thereafter; it does not exclude other elements or steps. It needs to be interpreted as specifying the presence of the stated features, integers, steps or components as referred to, but does not preclude the presence or addition of one or more other features, integers, steps or components, or groups thereof. Thus, the scope of the expression “a composition comprising A and B” should not be limited to the composition consisting only of A and B. It means that with respect to the present invention, the only compositional components of the composition are A and B. Accordingly, the terms “comprising” and “including” encompass the more restrictive terms “consisting essentially of” and “consisting of”.

As used herein, the terms "optional" or "optionally" means that a subsequently described event or circumstance can or cannot occur, and that the description includes instances where said event or circumstance occurs and instances where it does not.

Thus, the composition [composition (C), herein after] according to the present invention is for use in a steel making process.

In other words, the present invention relates to a composition (C) suitable to be used as a raw material in a steel making process. Within the context of the present invention, the expression “steel making process”, refers to a process for producing steel. Non-limiting examples of such steel making process are basic oxygen furnace (BOF) process, electric arc furnace (EAF) process and argon oxygen decarburization process (AOD). Preferably, the composition (C) is particularly suitable to be used as a raw material in an electric arc furnace (EAF) process.

As said, the composition according to the present invention is prepared from at least one steel scale by-product [compound SSB, herein after].

Within the context of the present invention, the expression "at least one steel scale by-product [compound SSB, herein after]” is intended to denote one or more than one steel scale by-product. Mixtures of steel scale by-product can also be used for the purpose of the invention. In the remainder of the text, the expression “steel scale by-product” is understood, for the purposes of the present invention, both in the plural and the singular form.

Within the context of the present invention, the compound (SSB) is intended to refer to a by-product, also called a waste, of a steel making process.

Scale is formed on the surface of steel during their high temperature thermal treatments after casting. In general, at the end of a steel making process, steel is immersed in an acidic bath (also called pickling process) to remove scale present at the surface of the steel. The acidic solution is then collected. Thereafter, lime is added to this acidic solution to reach a pH of about 10 and to precipitate dissolved metals. The resulting sludge which contained the precipitated metals is collected and subjected to a press process in order to separate the solid phase from the liquid phase. The solid phase comprises at least metals such as iron (Fe), chromium (Cr), nickel (Ni), molybdenum (Mo). In general, this solid phase also comprises a high content of moisture and is also called steel scale by-product, steel scale waste or filter cake.

Preferably, the compound (SSB) is a by-product from stainless steel process or carbon steel process or mixture thereof.

Advantageously the compound (SSB) can be in different forms such as a paste, a powder, scraps or mixture thereof. Preferably, the compound (SSB) is a paste. The compound (SSB) can also be chunked, milled, crushed or powdered.

As said, according to the present invention, said at least one steel scale by-product [compound (SSB), herein after] comprises equal to or more than 35.0 wt. % of free water, relative to the total weight of the compound (SSB).

Within the context of the present invention, the expression “free water” is intended to refer to the portion of water which evaporates upon heating. On the contrary, in general, the expression “bound water” refers to the water which remains bounded to the compound upon heating. It is understood that the skilled person in the art will measure the amount of free water according to standard and general practice known by said skilled person in the art. Preferably, unless otherwise mentioned or indicated, according to the present invention, the measurement of free water is performed by subjecting the sample to a heating step at 80 °C. According to the present invention, the free water is measured according to the standard NF 94-050 09-1995 at a heating step of 80 °C. In other words, the free water is measured according to the standard NF 94-050 09-1995 except that the heating step is performed at 80 °C instead of 50 °C or 105 °C. In general, the duration of the heating step is of at least 4h. It is further understood that the upper limit of the duration of the heating step is dependent on various parameters such as the content of free water in the sample and the nature of the sample. In general, the measurement of free water is performed until a constant weight of the sample subjected to said measurement is reached as described in the standard NF 94-050 09-1995

In general, said compound (SSB) comprises, or equal to or more than 40.0 wt. %, or equal to or more than 45.0 wt. %, or equal to or more than 50.0 wt. %, or equal to or more than 55.0 wt. %, of free water, relative to the total weight of the compound (SSB).

It is further understood that the upper limit of free water in the compound (SSB) is advantageously equal to or less than 80.0 wt. %, or equal to or less than 75.0 wt. %, or equal to or less than 70.0 wt. %, relative to the total weight of the compound (SSB).

In an embodiment of the composition of the present invention, free water, as detailed above, is present in the compound (SSB) in an amount from 35.0 wt. % to 80.0 wt. %, or from 35.0 wt. % to 75.0 wt. %, or from 40.0 wt. % to 75.0 wt. % or from 45.0 wt. % to 75.0 wt. %, or from 50.0 wt. % to 70.0 wt. % or from 55.0 wt. % to 70.0 wt. %, relative to the total weight of the compound (SSB).

The compound (SSB) may further comprise equal to or more than 0.2 wt. % of fluorine, expressed as CaF_2, relative to the total dry weight of the compound (SSB).

It is further understood that the expression “fluorine” also refers to the ionic form, F^-, fluoride.

Within the context of the present invention, unless otherwise mentioned or indicated, the expression “dry weight” is intended to refer to the weight of the compound (SSB) after the evaporation of the free water, as detailed above.

In general, the presence of fluorine, expressed as CaF_2, in the compound (SSB) may come from the steel making process from which the steel scale by-product is derived. In general, during the addition of lime to neutralize the acidic solution, CaF_2 is produced. Its content in the compound (SSB) is thus dependent on the conditions used during the steel making process from which the steel scale by-product is derived.

In general, said compound (SSB) may comprise equal to or more than 1.0 wt. %, or equal to or more than 5.0 wt. %, or equal to or more than 7.0 wt. %, of fluorine, expressed as CaF_2, relative to the total dry weight of the compound (SSB).

It is further understood that the upper limit of fluorine, expressed as CaF_2, in the compound (SSB) may advantageously be equal to or less than 15.0 wt. %, or equal to or less than 12.0 wt. %, or equal to or less than 10.0 wt. %, or equal to or less than 8.0 wt. %, relative to the total dry weight of the compound (SSB).

In an embodiment of the composition of the present invention, fluorine, expressed as CaF_2, as detailed above, is present in the compound (SSB) in an amount from 0.2 wt. % to 15.0 wt. %, or from 1.0 wt. % to 12.0 wt. %, or from 5.0 wt. % to 10.0 wt. %, relative to the total dry weight of the compound (SSB).

Preferably, the compound (SSB) can further comprise metals such as iron (Fe), chromium (Cr), nickel (Ni), molybdenum (Mo).

According to the present invention, the compound (SSB) may further comprise iron, expressed as Fe_2O_3, in an amount equal to or more than 10 wt. %, preferably equal to or more than 20 wt. %, equal to or more than 30 wt. %, relative the total dry weight of the compound (SSB). It is further understood that the expression “iron” refers to iron in all its forms (ionic forms) present in the compound (SSB).

In an embodiment of the composition of the present invention, the upper limit of iron, expressed as Fe_2O_3, in the compound (SSB) is equal to or less than 60 wt. %, preferably equal to or less than 50 wt. %, equal to or less than 60 wt. %, relative the total dry weight of the compound (SSB).

Preferably, iron, expressed as Fe_2O_3, is preferably present in the compound (SSB) in an amount from 10 wt.% to 60 wt. %, preferably from 20 wt. % to 50 wt. %, preferably from 30 wt. % to 40 wt. %, relative the total dry weight of the compound (SSB).

According to the present invention, the compound (SSB) may further comprise chromium in an amount equal to or more than 0.02 wt. %, preferably equal to or more than 0.06 wt. %, preferably equal to or more than 0.10 wt. %, relative the total dry weight of the compound (SSB).

In an embodiment of the composition of the present invention, the upper limit of chromium in the compound (SSB) is equal to or less than 15.0 wt. %, preferably equal to or less than 12.0 wt. %, equal to or less than 10.0 wt. %, relative the total dry weight of the compound (SSB).

Preferably, chromium is present in the compound (SSB) in an amount from 0.02 wt. % to 15.0 wt.%, or from 0.06 wt.% to 12.0 wt. %, preferably from 0.1 wt. % to 10 wt. %, relative the total dry weight of the compound (SSB).

According to the present invention, the compound (SSB) may further comprise nickel in an amount equal to or more than 0.02 wt. %, preferably equal to or more than 0.06 wt. %, preferably equal to or more than 0.1 wt. %, relative the total dry weight of the compound (SSB).

In an particular embodiment, the upper limit of nickel in the compound (SSB) is equal to or less than 15.0 wt. %, preferably equal to or less than 12.0 wt. %, preferably equal to or less than 10.0 wt. %, relative the total dry weight of the compound (SSB).

Preferably, nickel is present in the compound (SSB) in an amount from 0.02 wt. % to 15.0 wt.%, or from 0.06 wt.% to 12.0 wt. %, preferably from 0.1 wt. % to 10 wt. %, relative the total dry weight of the compound (SSB).

According to the present invention, the compound (SSB) may further comprise molybdenum in an amount equal to or more than 0.02 wt. %, preferably equal to or more than 0.05 wt. %, preferably equal to or more than 0.1 wt. %, relative the total dry weight of the compound (SSB).

In an embodiment of the composition of the present invention, the upper limit of molybdenum in the compound (SSB) is equal to or less than 15.0 wt. %, preferably equal to or less than 12.0 wt. %, preferably equal to or less than 10 wt. %, relative the total dry weight of the compound (SSB).

Preferably, molybdenum is present in the compound (SSB) in an amount from 0.02 wt. % to 15.0 wt.%, or from 0.06 wt.% to 12.0 wt. %, preferably from 0.1 wt. % to 10 wt. %, relative the total dry weight of the compound (SSB).

Preferably, chromium, nickel and molybdenum are present in the compound (SSB) in a cumulated amount from 0.1 wt. % to 50 wt. %, preferably from 0.2 wt. % to 40 wt. %, preferably from 0.5 wt. % to 30 wt. % relative to the total dry weight of the compound (SSB).

As said, the composition (C), as detailed above, is prepared by mixing the compound (SSB), as detailed above, with at least one first additive.

First additive

Within the context of the present invention, the expression "at least one first additive" is intended to denote one or more than one first additive. Mixtures of first additive can also be used for the purpose of the invention. In the remainder of the text, the expression "first additive" is understood, for the purposes of the present invention, both in the plural and the singular form.

As said, the composition (C), as detailed above, is prepared by mixing the compound (SSB), as detailed above, with at least one first additive in an amount providing a weight ratio of calcium oxide to the free water present in the compound (SSB) equal to or more than 1.50.

In other words, the first additive is mixed with the compound (SSB) in such a way to have a weight ratio of calcium oxide to free water of the compound (SSB) equal to or more than 1.50; $wt.\frac{\text{CaO (calcium based additive)}}{\text{free water (SSB)}} \geq 1.50.$

It is further understood that the lower limit of the amount of the first additive which is mixed with the compound (SSB) should be sufficient to provide the amount of calcium oxide, as detailed above.

Advantageously, the first additive is mixed with the compound (SSB) in an amount providing a weight ratio of calcium oxide to the free water present in the compound (SSB) equal to or more than 1.75, preferably equal to or more than 1.80, more preferably equal to or more than 1.90, even more preferably equal to or more than 2.00.

Advantageously, the first additive is mixed with the compound (SSB) in an amount providing a weight ratio of calcium oxide to the free water present in the compound (SSB) equal to or less than 2.50, preferably equal to or less than 2.25, more preferably equal to or less than 2.15 even more preferably equal to or less than 2.10.

In a preferred embodiment of the method of the present invention, the first additive is advantageously mixed with the compound (SSB) in an amount providing a weight ratio of calcium oxide to the free water present in the compound (SSB) from 1.50 to 2.50, more preferably from 1.80 to 2.25, most preferably from 2.0 to 2.15.

According to the present invention, the first additive comprises calcium oxide in an amount of at least 80.0 wt. %, relative to the total weight of the first additive. In other words, the expression “first additive” is intended to refer to a compound comprising at least 80.0 wt. % of calcium oxide or a composition comprising at least 80.0 wt. % of calcium oxide or a mixture thereof.

Advantageously, the first additive comprises calcium oxide in an amount of at least 85.0 wt. %, preferably in an amount of at least 90.0 wt. %, more preferably in an amount of at least 95.0 wt. %, even more preferably in an amount of at least 98.0 wt. %, relative to the total weight of the first additive.

According to a preferred embodiment of the composition of the present invention, the first additive is a compound comprising or consisting essentially of calcium oxide, as detailed above, wherein the total amount of the calcium oxide is equal to or more than 80.0 wt.%, or more than 85.0 wt.% or more than 90.0 wt.% or more than 95.0 wt.% or desirably more than 98.0 wt.% relative to the total weight of the compound.

In general, the skilled in the art knows how to select the first additive to provide the weight ratio as detailed above.

According to the present invention, the first additive may further comprise at least one calcium salt, other than calcium oxide, in an amount equal to or less than 20 wt. %, preferably equal to or less than 15 wt. %, more preferably equal to or less than 10 wt. %, relative to the total weight the first additive. Within the context of the present invention, the expression “at least one calcium salt” is intended to denote one or more than one calcium salt. In the rest of the text, the expression “at least one calcium salt” is understood, for the purposes of the present invention, both in the plural and the singular. Non-limiting examples of such calcium salts are calcium carbonate, calcium hydroxide, calcium sulfate, or calcium nitrate.

According to an embodiment of the present invention, the first additive may further comprise at least one magnesium salt selected from the group consisting of magnesium carbonate, magnesium oxide, and magnesium hydroxide. Within the context of the present invention, the expression “at least one magnesium salt” is intended to denote one or more than one magnesium salt. In the rest of the text, the expression “at least one magnesium salt” is understood, for the purposes of the present invention, both in the plural and the singular.

In this embodiment, the content of magnesium, expressed as magnesium oxide, present in the first additive is equal to or less than 10.0 wt. %, preferably equal to or less than 7.0 wt. %, more preferably equal to or less than 5.0 wt. %, relative to the total weight of the first additive.

The first additive according to the present invention may further comprise impurities in an amount equal to or less than 5.0%, preferably equal to or less than 4.0 wt. %, more preferably equal to or less than 2.5 wt. %, relative to the total weight of the first additive. Non limiting examples of such impurities are silicon, aluminum, iron, sodium, potassium, sulfur, phosphorous alone or in combination. The impurities may also be in salt form, in oxide form, in combination with calcium or combination thereof.

Said first additive may be a compound or a composition or mixture thereof.

Said first additive may be synthetically prepared by a variety of methods known in the art or can be of natural origin.

Non-limiting examples of first additive of natural origin may be made from mined (raw) minerals such as limestones. In general, limestone comprises $CaCO_3$ in a total amount of more than 95.0 wt.%, or more than 96.0 wt.%, or more than 97.0 wt.%, or desirably more than 98.0 wt.%, relative to the total weight of the limestone.

In a preferred embodiment of the invention, the first additive is a quicklime. In general quicklime is made from limestones, in particular by calcining limestones.

In this embodiment, when the first additive is a quicklime, said quicklime has a reactivity, t_{60}, of at most 10 minutes. The quicklime reactivity is evaluated with the European reactivity on slaking test, EN 459-2: Building lime – Part 2: Tests methods. In general, the quicklime reactivity is expressed as t_{60}, which is the time needed to reach 60 °C when 150 g of quicklime is added to 600 cm^3 of water. Preferably, the quicklime complies with the chemical requirements of a calcium lime CL80-R5 according to the European standard EN 459-1.

The inventors have now found that when the composition (C) is prepared by mixing the compound (SSB), as detailed above, with the at least one first additive, as detailed above, in an amount providing a weight ratio of calcium oxide to the free water present in the compound (SSB) equal to or more than 1.50, the free water of the resulting composition (C) is significantly reduced.

According to the present invention, the composition (C), after mixing the compound (SSB), as detailed above, with the at least one first additive, as detailed above, comprises free water in an amount equal to or less than 5.0 wt. %, relative to the total weight of the composition (C).

The inventors have found that the composition (C) of the present invention, can be safely used in a steel making process. A free water equal to or less than 5 wt. % in the composition (C) is an important figure as this is the threshold for safely reintroducing this composition as a raw material in a steel making process. Indeed, a low content of free water in the raw material is mandatory in a steel making process to avoid rapid expansion of the free water into gas. Due to the high temperatures used in a steel making process, the free water becomes a gas which takes up a greater volume. This rapid expansion of the liquid water into a gas can be so sudden that the liquid steel is ejected out of the vessel. This causes a major safety risk and potentially damages equipment. Therefore, the use of the first additive according to the invention is cost-effective since it avoids the use of further drying steps. Moreover, it allows the recycling and the reuse of the by-product, notably of the high value metals and alloys that are contained in the compound (SSB).

The present invention provides a solution for the recovering and recycling of steel scale by-product and facilitating the subsequent reuse of this by-product in a steel making process while improving the performance of this process. In view of the public policies favoring recycling, notably in the steel making field, the present invention has an important economic potential.

It is further understood that the definition of free water, as described above for the compound (SSB), equally applies for the composition (C).

Preferably, said composition (C) comprises equal to or less than 4.5 wt. %, equal to or less than 4.0 wt. %, preferably equal to or less than 3.5 wt. %, more preferably equal to or less than 3.0 wt. %, most preferably equal to or more than 2.5 wt. %, most preferably equal to or more than 2.0 wt. %, even more preferably equal to or less than 1.5 wt. %, of free water relative to the total weight of the composition (C).

It is further understood that the lower limit of free water in the composition (C) is advantageously equal to or more than 0.0 wt. % or equal to or more than 0.2 wt. %, preferably equal to or more than 0.3 wt. %, preferably equal to or more than 0.4 wt. %, more preferably equal to or more than 0.5 wt. %, even more preferably equal to or more than 0.7 wt. %, most preferably equal to or more than 1.0 wt. %, relative to the total weight of the composition (C).

In an embodiment of the composition of the present invention, free water, as detailed above, is advantageously present in the composition (C) in an amount from 0.0 wt. % to 5.0 wt. %, preferably from 0.2 wt. % to 4.5 wt. %, preferably from 0.3 wt. % to 4.0 wt. %, more preferably from 0.5 wt. % to 3.5 wt. %, more preferably from 0.7 wt. % to 3.0 wt. % from 1.0 wt. % to 3.0 wt. % or from 1.0 wt. % to 2.0 wt. %, relative to the total weight of the composition (C).

Advantageously, according to the present invention, the composition (C), after mixing the compound (SSB), as detailed above, with the at least one first additive, as detailed above, further comprises fluorine, expressed as CaF_2, in an amount equal to or less than 20.0 wt.%, preferably equal to or less than 15.0 wt.

%, preferably equal to or less than 10.0 wt. %, relative to the total dry weight of the composition (C).

It is further understood that the definition of dry weight, as described above for the compound (SSB), equally applies for the composition (C).

According to a certain embodiment of the invention, a second additive may be added to the composition (C), as detailed above, wherein said second additive is comprising, relative to the total weight of said second additive, at least 20.0 wt. % of magnesium, expressed as magnesium oxide.

The amount added to the composition (C), as detailed above, is determined by the amount of fluorine, expressed as CaF_2, in the composition (C) and the nature of the second additive.

Advantageously, the second additive is added in an amount providing in the composition (C) a weight ratio of magnesium, expressed as magnesium oxide, to fluorine, expressed as CaF_2, equal to or more than 5.0.

Second additive

Within the context of the present invention, the expression “at least on second additive” is intended to denote one or more than one second additive. Mixtures of second additive can also be used for the purpose of the invention. In the remainder of the text, the expression “second additive” is understood, for the purposes of the present invention, both in the plural and the singular form.

Within the context of the present invention, the expression “second additive” is intended to refer to a compound comprising at least one magnesium salt or a composition comprising at least one magnesium salt or a mixture thereof.

Within the context of the present invention, the expression “at least one magnesium salt” is intended to denote one or more than one magnesium salt.

In the rest of the text, the expression “at least one magnesium salt” is understood, for the purposes of the present invention, both in the plural and the singular.

Non-limiting examples of suitable magnesium salts may be made of magnesium carbonate, magnesium hydroxide, magnesium oxide, magnesium sulphate, magnesium silicate or magnesium nitrate.

According to a preferred embodiment of the composition of the present invention, the at least one magnesium salt is selected from the group consisting of magnesium carbonate, magnesium oxide, and magnesium hydroxide.

As said, the composition of the present invention, as detailed above, may be prepared by using at least one second additive in an amount providing in the composition (C) a weight ratio of magnesium, expressed as magnesium oxide, to fluorine, expressed as CaF_2, equal to or more than 5.0.

In other words, the second additive is used in such a way to have a composition (C) wherein the weight ratio of magnesium, expressed as magnesium oxide, to fluorine, expressed as CaF_2, is equal to or more than 5.0;

$$wt.\frac{\text{Mg,expressed as MgO (compo (C))}}{\text{Fluorine,expressed as } CaF_2 \text{(compo (C))}} \geq 5.0$$

In general, the skilled in the art knows how to determine the amount of the second additive needed to provide the weight ratio, as detailed above. The amount of the second additive is dependent on the content of magnesium in the second additive and on the fluorine, expressed as CaF_2, in the composition (C) after mixing the compound (SSB), as detailed above, with the at least one first additive, as detailed above.

In a certain embodiment of the present invention, the composition (C) is prepared by further adding the second additive in an amount from 400 wt. % to 2500 wt. %, preferably from 1000 wt. % to 2000 wt. %, preferably from 1500 wt.% to 1800 wt. %, relative to the weight of fluorine, expressed as CaF_2, in the composition, after mixing the compound (SSB), as detailed above, with the at least one first additive, as detailed above.

It is further understood that the lower limit of the amount of the second additive which is used should be sufficient to provide the content of magnesium, expressed as magnesium oxide, as detailed above.

Advantageously, the second additive is used in an amount providing in the composition (C) a weight ratio of magnesium, expressed as magnesium oxide, to fluorine, expressed as CaF_2, equal to or more than 7.0, preferably equal to or greater than 10.0, more preferably equal to or greater than 12.0, most preferably equal to or greater than 15.0, even more preferably equal to or greater than 20.0.

Advantageously, the second additive is used in an amount providing in the composition (C) a weight ratio of magnesium, expressed as magnesium oxide, to fluorine, expressed as CaF_2, equal to or less than 25.0, preferably equal to or less than 20.0, more preferably equal to or less than 15.0, most preferably equal to or less than 12.0, even more preferably equal to or less than 10.0.

In a preferred embodiment of the method of the present invention, the second additive is used in an amount providing in the composition (C) a weight ratio of magnesium, expressed as magnesium oxide, to fluorine, expressed as CaF_2, from 5.0 to 25.0, preferably from 7.0 to 20.0, more preferably from 10.0 to 15.0, most preferably from 12.0 to 15.0, or from 7.0 to 10.0.

According to the present invention, said second additive comprises magnesium, expressed as magnesium oxide, in an amount of at least 20.0 wt. %, relative to the total weight of the second additive. In general, the skilled in the art knows how to select the second additive to provide the weight ratio as detailed above.

According to a preferred embodiment of the composition of the present invention, the second additive comprises or consists essentially of a magnesium salt, as detailed above, wherein the total amount of magnesium, expressed as magnesium oxide, is of at least at least 25.0 wt.%, or of at least 30.0 wt.%, or of at least 35.0 wt. %, or desirably of at least 35.0 wt.% relative to the total weight of the second additive. Advantageously, the magnesium content, expressed as magnesium oxide, is less than 90.0 wt.%, or less than 80.0 wt.%, or less than 70.0 wt.%, or less than 60.0 wt.%, or less than 55.0 wt.%, or less than 50.0 wt.%, or desirably less than 45.0 wt.%, relative to the total weight of the second additive.

According to a preferred embodiment of the composition of the present invention, the second additive may further comprise at least one calcium salt selected from the group consisting of calcium carbonate, calcium oxide, and calcium hydroxide.

According to a preferred embodiment of the composition of the present invention, the second additive comprises or consists essentially of the magnesium salt, as detailed above and the calcium salt, as detailed above, wherein the total amount of magnesium, expressed as magnesium oxide, and calcium, expressed as calcium oxide, is more than 80.0 wt.%, or more than 85.0 wt.% or more than 90.0 wt.% or more than 95.0 wt.% or desirably more than 98.0 wt.% relative to the total weight of the compound, and wherein the magnesium content, expressed as magnesium oxide, is of at least 20.0 wt.%, or of at least 25.0 wt.%, or desirably of at least 30.0 wt.%, relative to the total weight of the second additive. Advantageously, the magnesium content, expressed as magnesium oxide, is less than 90.0 wt.%, or less than 80.0 wt.%, or less than 70.0 wt.%, or less than 60.0 wt.%, or less than 55.0 wt.%, or less than 50.0 wt.%, or desirably less than 45.0 wt.%, relative to the total weight of the second additive. Advantageously, the calcium content, expressed as calcium oxide, is less than 80.0 wt.%, or less than 70.0 wt.%, or less than 60.0 wt.%, or less than 50.0 wt.%, or less than 40.0 wt.%, or less than 30.0 wt.%, or desirably less than 20.0 wt.%, relative to the total weight of the second additive.

Desirably, the magnesium content, expressed as magnesium oxide, varies from 20.0 wt.% to 80.0 wt.%, or from 20.0 wt.% to 70.0 wt.%, or from 25.0 wt.% to 60.0 wt.% or from 30.0 wt.% to 50.0 wt.%, or from 30.0 wt.% to 45.0 wt.%, relative to the total weight of the second additive.

Said second additive may be synthetically prepared by a variety of methods known in the art or can be of natural origin.

Non-limiting examples of second additive of natural origin may be made of mined (raw) minerals such as dolomite and dolomitic limestones.

In general, dolomitic limestone comprises $MgCO_3$ and $CaCO_3$, in which the $MgCO_3$ and $CaCO_3$ are present in a total amount of more than 95.0 wt.%, or more than 96.0 wt.%, or more than 97.0 wt.%, or desirably more than 98.0 wt.%, relative to the total weight of the dolomitic limestone, and wherein the MgCO3 content may vary from 20.0 wt.% to 45.0 wt.%, or from 25.0 wt.% to 40.0 wt.%, or from 30.0 wt.% to 40.0 wt.% relative to the total weight of $MgCO_3$ and $CaCO_3$.

In general, dolomite comprises $MgCO_3$ and $CaCO_3$, in which the $MgCO_3$ and $CaCO_3$ are present in a total amount of more than 95.0 wt.%, or more than 96.0 wt.%, or more than 97.0 wt.%, or desirably more than 98.0 wt.%, relative to the total weight of the dolomitic limestone, and wherein the $MgCO_3$ and $CaCO_3$ content are present in a 1:1 molar ratio.

Non-limiting examples of synthetically prepared second additive suitable to be used in the composition of the present invention may be partly or fully burnt dolomite consisting of calcium oxide and magnesium oxide (also called calcined dolomite or dolomitic quick lime or dolime), calcium hydroxide and magnesium oxide (also called semi-hydrated dolomitic lime) or calcium hydroxide and magnesium hydroxide (also called type S hydrated lime).

Alternatively, the second additive consists essentially of at least one magnesium salt, as detailed above.

Within the context of the present invention, the term “consisting essentially of” is to be understood to mean that any additional component different from the magnesium salt, as detailed above, is present in an amount of at most 1.0 wt.%, or at most 0.5 wt.%, or at most 0.1 wt.%, based on the total weight of the second additive. Non-limiting examples of such additive are magnesia, magnesite, olivine and brucite.

It is further understood that the first additive and the second additive according to the present invention are two different compounds or compositions.

The inventors have surprisingly found that when a second additive, as detailed above, is used to prepare the composition (C), as detailed above, the negative impact of CaF_2 on the slag viscosity during the steel making process is reduced. It has been found that CaF_2 is a slag fluidizer. This means that when a composition containing a high quantity of CaF_2 is used as raw material in a steel making process, the viscosity of the slag generated during the process is low. This slag having a low viscosity no longer correctly covers the liquid steel which results in a reduction of the thermal insulation and increases the risk of nitrogen pick that can then reduce the yield for the process. Therefore, the use of the second additive according to the invention results in an improvement of the yield of the steel making process while using a by-product as raw material.

According to the present invention, the composition (C), after mixing the compound (SSB), as detailed above, with the at least one first additive, as detailed above, and with the at least one second additive, as detailed above, further comprises fluorine, expressed as $CaF_{2,}$ in an amount equal to or less than 10.0 wt. %, relative to the total dry weight of the composition (C).

The inventors have thus found that the composition (C) of the present invention, can be safely used as raw material in a steel making process and that the yield of said process is improved and the need of further additives during the process is reduced.

It is further understood that the definition of dry weight, as described above for the compound (SSB), equally applies for the composition (C).

Preferably, said composition (C) comprises equal to or less than 8.0 wt. %, equal to or less than 7.0 wt. %, preferably equal to or less than 6.0 wt. %, more preferably equal to or less than 5.0 wt. %, even more preferably equal to or less than 4.0 wt. %, most preferably equal to or less than 3.0 wt. %, most preferably equal to or less than 2.0 wt. %, of fluorine, expressed as $CaF_{2,}$ relative to the total dry weight of the composition (C).

It is further understood that the lower limit of fluorine, expressed as $CaF_{2,}$ in the composition (C) is advantageously equal to or more than 0.0 wt. % or equal to or more than 0.2 wt. %, preferably equal to or more than 0.5 wt. %, preferably equal to or more than 0.7 wt. %, more preferably equal to or more than 1.0 wt. %, even more preferably equal to or more than 1.5 wt. %, most preferably equal to or more than 2.0 wt. %, relative to the total dry weight of the composition (C).

In an embodiment of the composition of the present invention, fluorine, expressed as $CaF_{2,}$, as detailed above, is advantageously present in the composition (C) in an amount from 0.0 wt. % to 10.0 wt. %, preferably from 0.2 wt. % to 8.0 wt. %, preferably from 0.5 wt. % to 7.0 wt. %, more preferably from 0.7 wt. % to 6.0 wt. %, more preferably from 1.0 wt. % to 5.0 wt. % or from 1.5

wt. % to 5.0 wt. % or from 2.0 wt. % to 5.0 wt. %, relative to the total dry weight of the composition (C).

Preferably, said composition (C) further comprises at least one shaping agent. In general, the skilled in the art knows how to select the shaping agent to improve the shaping step. Indeed, the shaping agent allows the various components as comprised in the composition (C), as detailed above, to be bound together, to improve the shaping step and the mechanical properties of the resulting shaped composition (C).

Within the context of the present invention, the expression “at least one shaping agent” is intended to denote one shaping agent or more than one shaping agent. Mixtures of shaping agent may be used.

In the rest of the text, the expression “shaping agent” is understood, for the purposes of the present invention, both in the plural and the singular form.

Non limiting examples of shaping agent are compounds comprising at least one saccharide and compounds comprising at least on stearic acid salt. Non-limiting examples of compounds comprising at least one saccharide are sugar and molasses.

Non-limiting examples of stearic acid salt are stearic acid sodium salt, stearic acid calcium salt, stearic acid magnesium salt, stearic acid zinc salt and stearic acid aluminum dihydroxide salt. Stearic acid calcium salt is especially preferred.

Preferably, said at least one shaping agent comprises at least 30.0 wt.% of at least one saccharide (S) selected from the group consisting of a mono-, di-, tri-, and tetra-saccharide [hereinafter saccharide (S)], relative to the total weight of the shaping agent.

Within the context of the present invention, the expression “at least one saccharide selected from the group consisting of a mono-, di-, tri-, and tetra-saccharide [hereinafter saccharide (S)],” is intended to denote one saccharide (S) or more than one saccharide (S). Mixtures of saccharide (S) may be used.

In the rest of the text, the expression “saccharide (S)” is understood, for the purposes of the present invention, both in the plural and the singular form.

Within the context of the present invention, the term “saccharide” as used herein, may have the broadest meaning generally known in the art.

The saccharide (S) may contain one carbohydrate unit or more than one carbohydrate unit, said more than one carbohydrate unit may be identical or independently different from each other.

The saccharide (S), as defined above, may also contain one or more carbohydrate unit containing five or six carbon atoms, which is respectively referred to as pentose and hexose.

Non-limiting examples of pentoses mention may be made of ribose, arabinose, arabulose, lyxose, lyxulose, ribulose, xylose, and xylulose, optionally substituted with at least one halo, C_{1-6} alkyl or C_{1-6} alkoxy substituent.

Non-limiting examples of hexoses mention may be made of allose, altrose, fructose, galactose, glucose, gulose, idose, mannose, psicose, sorbose, tagatose, and talose, optionally substituted with at least one halo, C_{1-6} alkyl or C_{1-6} alkoxy substituent.

According to a preferred embodiment of the present invention, the saccharide (S) is selected from the group consisting of monosaccharide and disaccharide.

Preferred monosaccharides are selected from the group consisting of glucose, mannose, fructose, galactose, ribose, arabinose, and xylose, more preferably, the saccharide (S) is selected from the group consisting of glucose, mannose and fructose.

Preferred disaccharides are selected from the group consisting of sucrose, lactose, maltose, trehalose, and cellobiose, more preferably from the group consisting of sucrose, lactose and maltose. Sucrose is especially preferred.

According to a more preferred embodiment of the present invention, the saccharide (S) product is selected from the group consisting of glucose, mannose, fructose and sucrose. Sucrose is especially preferred.

Preferably, the at least one shaping agent comprises at least 40.0 wt.%, more preferably, at least 50.0 wt.%, even more preferably at least 60.0 wt.%, most preferably 70.0 wt.%, more preferably at least 75 wt.% of at least one saccharide (S), as detailed above, relative to the total weight of the shaping agent.

In general, the skilled in the art knows how to determine the amount of the shaping agent to improve the shaping step, as detailed above. Preferably, the composition (C) of the present invention, relative to the total weight of the composition (C), comprises at least 1.0 wt.%, or at least 1.5 wt.%, or at least 2.0 wt.%, or at least 2.5 wt.% of the shaping agent, as detailed above.

It is further understood that the upper limit of the shaping agent in the composition (C) is advantageously equal to or less than 8.0 wt. % or equal to or more than 7.0 wt. %, preferably equal to or more than 6.5 wt. %, preferably equal to or more than 6.0 wt. %, more preferably equal to or more than 5.5 wt. %, even more preferably equal to or more than 5.0 wt. %, relative to the total weight of the composition (C).

In an embodiment of the composition of the present invention, shaping agent, as detailed above, is advantageously present in the composition (C) in an amount from 1.0 wt. % to 8.0 wt. %, preferably from 1.5 wt. % to 7.0 wt. %, preferably from 2.0 wt. % to 6.5 wt. %, more preferably from 2.0 wt. % to 6.0 wt. %, more preferably from 2.5 wt. % to 6.0 wt. % or from 2.5 wt. % to 5.5 wt. % or from 2.0 wt. % to 5.0 wt. %, relative to the total weight of the composition (C).

Preferably, the composition (C) is in the form of a solid composition. For the purpose of the present invention, the term “solid composition” is intended to refer to a composition in the form of powders, fibers, dusts, tablets, pellets, aggregates, compacts or briquettes or a granular form such as granules or crumbs,.

Preferably, said composition (C), is in a form selected from the group consisting of powders, aggregates, briquettes or mixtures of two or more thereof. Preferably, said composition (C) is in a form selected from the group consisting of aggregates, briquettes or mixtures of two or more thereof.

Method for manufacturing the composition (C)

The methods to manufacture composition (C) are also an aspect of the present invention.

It is further understood that all definitions and preferences, as described above, equally apply for all further embodiments, as described below.

The composition (C) of the present invention can be prepared by a variety of methods known in the art.

In one embodiment of the present invention, the method for the manufacturing of the composition (C), as detailed above, comprises mixing of **(a)** at least one compound (SSB), as detailed above, **(b)** at least one first additive, as detailed above and **(c)** optionally at least one second additive, as detailed above.

The inventors have further found that the composition (C) prepared according to the invention is particularly suitable for use as raw material in a steel making process.

It is understood that the skilled person in the art will carry out said mixing according to general practice such as notably using optimal times, speeds, weights, volumes and batch quantities.

Furthermore, it is understood that any order of mixing of the various components as comprised in the composition (C), as detailed above, is acceptable.

When appropriate, the first additive, as detailed above and the second additive, as detailed above, can be pre-mixed to form a premix prior to the mixing with the compound (SSB), or the first additive and the second additive can be separately mixed with the compound (SSB).

When the first additive and the second additive are separately mixed with the compound (SSB), the first additive and the second additive can be mixed simultaneously, or, if desired, the second additive can be mixed after the first additive.

It is further understood that the various components as comprised in the composition (C), as detailed above may be introduced in the solid form or in the liquid form. Non-limiting examples of solid form are a powder or dust, however, it may also be present in a compressed form such as tablets, pellets or granules to manufacture the composition (C).

The form of the various compounds as comprised in the composition (C), as detailed above is generally known to the person skilled in the art.

The the various components as comprised in the composition (C) are generally in a solid form, as detailed above, however, it may also be present in a solution.

For example, when molasses is used as shaping agent, this compound is a liquid, namely a viscous liquid.

Generally said mixing, as detailed above, may be carried out by using a variety of mixing means known in the art. Non-limiting examples of such mixing means are for example mechanical mixing such as traditional mixers and blenders, high intensity mixers and electric stirrers, said mixers, blenders and stirrers which can be equipped with at least one dispersion disk. A high sheer force can be applied during the mixing in order to improve the homogeneity of the composition (C).

Preferably, said mixing is carried out until a homogeneous mixture is obtained.

Advantageously, the composition (C) may be further converted into a pellet form, tablet form, briquette form, compact form, aggregate form or granular form, or mixtures thereof. Such conversion methods are known in the art.

In a preferred embodiment, said composition (C), after mixing, is then subjected to a shaping step. In general during this shaping step, a shape is given to the composition (C). Various shaping process are known in the art and non-limiting examples of such a shaping process are pelletizing, compacting, slip casting, aggregating, extrusion. Preferably, the shaping process is a compacting process. Non-limiting examples of compacting processes are cold isostatic pressing, tabletting, briquetting, roll compaction. After the shaping process, the shaped composition (C) can take various forms such as compacts, tablets, briquettes, pellets, extrudates.

Preferably, according to the invention, the shaped composition (C) takes the form of briquettes or aggregates.

Preferably, according to the invention, there is a latency step between the mixing and the shaping step.

Advantageously, the duration of said latency step is of at least 6h, preferably, at least 12h, more preferably at least 18h, even more preferably at least 20h, most preferably at least 24h.

In a preferred embodiment of the invention, said shaping agent is added in the composition (C) after the mixing, as detailed above, and before the shaping step, as detailed above.

When the process comprises a latency step, said shaping agent may be added before and/or during and/of after said latency step. The addition of the shaping agent after the latency step and before the shaping step is especially preferred.

The premix of the first additive, as detailed above, and the second additive, as detailed above, is another aspect of the present invention.

It is further understood that all definitions and preferences, as described above, equally apply for the premix.

The use of the composition (C), as detailed above, as raw material in a steel making process is another aspect of the invention.

It is further understood that all definitions and preferences, as described above, equally apply for the use of the composition (C) as raw material in a steel making process.

EXAMPLES

The invention will be now described in more details with reference to the following examples, whose purpose is merely illustrative and not intended to limit the scope of the invention.

Test methods

Measurements of free water

The measurements of free water were performed by subjecting the sample to a heating step at 80 °C until a constant weight of the sample subjected to said measurement was reached.

Measurements of fluorine

The amount of fluorine was measured after the measurement of free water, described above. Fluorine was thus measured on a “dry sample”, after the evaporation of the free water, as detailed above.

The measurements of fluorine were performed by using wavelength dispersive X-ray fluorescence spectrometer device from Malvern Panalytical Zetium.

Measurements of the reactivity

The quicklime reactivity was evaluated with the European reactivity on slaking test, EN 459-2: Building lime – Part 2: Tests methods. The reactivity t_{60}, was determined as the time needed to reach 60 °C when 150 g of quicklime was added to 600 cm^3 of water.

Measurements of the LOI (Loss on ignition)

The LOI, in order to determine the amount of bound water and carbonate in the invention, was obtained using thermogravimetric analysis (TGA) performed by gradually raising the temperature of a sample of the composition, at a rate of 5°C/min from room temperature to at least 950°C (or to constant mass) in a furnace under a flow of nitrogen, as its weight was measured on an analytical scale. The weight of the sample was plotted against temperature to observe thermal transitions/decompositions that occur upon raising temperature. The hydrated compound(s) comprised in the composition of the invention decompose(s) between 350°C and 550°C by releasing water (then called “bound water”). The mass loss occurring between 350°C and 550°C corresponds therefore to the amount of “bound water” (expressed as H_2O) according to the invention. The carbonate compound(s) comprised in the composition of the invention decompose(s) between 550°C and 950°C (or constant mass) by releasing CO_2. The mass loss occurring between 550°C and 950°C (or constant mass) corresponds therefore to the amount of total carbonate (expressed as CO_2) according to the invention.

Measurements of the mechanical resistance of the agglomerated composition

The compressive strength was measured by applying a progressively increasing load (or force) on a solid sample until fracture. The maximum force applied before fracture was recorded and used as an indicator of the mechanical resistance.

The measurement was performed using a laboratory press Mecmesin OmniTest.

Example 1 (E1)

Example 1 was realized using the raw materials having the composition and properties as described in tables 1-3.

Table 1: Steel scale by-product compound (compound SSB)

	Wt. %
Free water *	55.0
CaF_2 **	36.2
Fe_2O_3 **	30.4
Cr **	5.3
Ni **	4.1
Mo **	0.1
* relative to the total weight of the compound SSB ** relative to the total dry weight of the compound SSB	

Table 2: First additive - composition

	Amount (wt. %*)
Na_2O	0.04
MgO	1.55
Al_2O_3	0.252
SiO_2	0.745
P_2O_5	0.025
SO_3	0.123
K_2O	0.046
CaO	92.94
Ti	0.032
Fe_2O_3	0.090
Zn	0.005

Sr	0.041
H_2O (bound water)	0.9
CO_2 (carbonate)	0.7
* Relative to the total weight of the first additive	

Table 3: First additive – reactivity

Reactivity	
T60 (min)	1.6
T°2' (°c)	63.2
Tmax (°c)	74.7

The compound SSB, described in table 1, was mixed with a first additive, as detailed in tables 2 and 3, in an amount providing a weight ratio of calcium oxide to the free water present in the compound (SSB) of 1.62. The mixing was performed with an Eirich intensive mixer type R01, at 300 rpm stirrer speed and 42 rpm bowl speed. 1.5 kg of compound SSB was add to the mixer together with 500g of the first additive, as detailed in table 1 and 2, and mixed during 30 min. Then, an additional 500g of first additive was added and mixed during 30 min. Then, an additional 500g of first additive was added and mixed during 30 min.
The resulting composition was sampled after 2h from the start to measure its free water content which was of 4.7 wt%, relative to the total weight of the composition. This result shows that the addition of the first additive allows to obtain a composition having a content of free water less than 5 wt. %, which can thus be used as raw material in a steel making process.

Example 2 (E2)

Example 2 was realized by mixing the composition obtained in example 1 with a second additive presenting the composition as detailed in table 4.

Table 4 : Second additive – composition

	Amount (wt. %*)
H_2O free	< 0.01
MgO	27.5
CaO	40.0
Fe_2O_3	1.8
F	< 0.01
SO_3	1.8
SiO_2	3.0
Total LOI (bound water + carbonate)	26.0
*relative to the total weight of the second additive	

The content of fluorine, expressed as CaF_2, in the composition obtained in example 1 was measured, as detailed above, and was of 8.8 wt. %, relative to the total dry weight of the composition. Then 216.6g of the second additive, as detailed in table 4, was added and mixed with 200g sampled from the composition obtained in example 1.

The mixing was performed using a WAB Turbula® mixer for 10 min at 72 rpm. The free water of the resulting composition was of 2.2 wt. %, relative to the total weight of the composition. In this composition, the weight ratio of the magnesium, expressed as magnesium oxide, to the fluorine, expressed as CaF_2, was 5.0. This result shows that the addition of the second additive allows to obtain a composition which can be safely used as raw material in a steel making process.

Comparative Example 3 (CE3)

The compound SSB, described in table 1, was mixed with a first additive, as detailed in tables 2 and 3, in an amount providing a weight ratio of calcium oxide to the free water present in the compound (SSB) of 1.1. The mixing was performed with a fast shear mixer as described in standard NF P 94-093. 1.5 kg of compound SSB was add to the mixer together with 500g of the first additive, as detailed in table 1 and 2, and mixed during 30 min. Then, an additional 500g of first additive was added and mixed during 30 min.

The resulting composition was sampled after 1h from the start to measure its free water content which was of 17.4 wt%, relative to the total weight of the composition. This result shows that the addition of the first additive in a lower ratio does not allow to obtain a composition which can be safely used as raw material in a steel making process.

Table 5 : Results

	E1	**E2**	**CE3**
Free water in composition (C)	4.7	2.2	17.4
Ratio CaO/Free H_2O during the addition of first additive	1.62	1.62	1.08
Ratio MgO/CaF_2 after addition of second additive	N/A	5.0	N/A

Example of shaping process

Example 4

Example 4 was realized using the composition obtained in example 1.

15g product was pressed at 94Mpa using a lab-scale tableting device to obtain an agglomerated composition in the form of a tablet which had a compressive mechanical strength of 890N. This result shows that the composition of the present can be shaped and that the resulting shaped product presents good mechanical strength.

CLAIMS

1. A method for manufacturing a composition for use as raw material in a steel making process [composition (C), herein after], which method comprises mixing of:

(a) at least one steel scale by-product [compound (SSB), herein after] which comprises equal to or more than 35.0 wt. % of free water, relative to the total weight of the compound (SSB);

(b) at least one first additive in an amount providing a weight ratio of calcium oxide to the free water present in the compound (SSB) equal to or more than 1.50, wherein said first additive comprises calcium oxide in an amount of at least 80.0 wt. %, relative to the total weight of the first additive;

wherein said composition (C) comprises free water in an amount equal to or less than 5.0 wt. %, relative to the total weight of the composition (C),

2. The method according to claim 1 which method further comprises mixing of:

(c) at least one second additive in an amount providing in the composition (C) a weight ratio of magnesium, expressed as magnesium oxide, to fluorine, expressed as CaF_2, equal to or more than 5.0, wherein said second additive comprises, relative to the total weight of the second additive, at least at least 20.0 wt. % of magnesium, expressed as magnesium oxide

wherein said composition (C) further comprises fluorine, expressed as CaF_2, in an amount equal to or less than 10.0 wt. %, relative to the total dry weight of the composition (C).

3. The method according to claim 1 or claim 2 wherein the compound (SSB) further comprises iron, expressed as Fe_2O_3, in an amount from 20 wt. % to 50 wt. %, relative the total dry weight of the compound (SSB).

4. The method according to any one of claims 1 to 3 wherein the compound (SSB) furthers comprise chromium, nickel and molybdenum in a cumulated amount from 0.5 wt. % to 30 wt. %, relative to the total dry weight of the compound (SSB).

5. The method according to any one of claims 1 to 4 wherein the first additive is a quicklime, preferably said quicklime as a reactivity, t60, of at most 10 minutes, wherein the reactivity is measured according to European reactivity on slaking test, EN 459-2.

6. The method according to any one of claims 2 to 5 wherein said at least one magnesium salt being selected from the group consisting of magnesium carbonate, magnesium oxide, and magnesium hydroxide.

7. The method according to any one of claims 1 to 6 wherein the second additive is selected from the group consisting of dolime, dolomite, magnesia, magnesite, olivine, brucite and mixtures of two or more thereof.

8. The method according to any one of claims 1 to 7 wherein said composition (C) is in a form selected from the group consisting of powders, aggregates, briquettes or mixtures of two or more thereof.

9. The method according to any one of claims 1 to 8 wherein the at least one first additive and the at least one second additive are premixed for forming a premix before mixing said at least one compound (SSB).

10. The method according to any one of claims 1 to 9 wherein said composition (C) is subjected to a shaping process after said mixing, preferably the shaping process is a compacting process.

11. The method according to claim 10 wherein the composition (C), after said shaping process, is in a shaped form selected from the group consisting of tablets, pellets, aggregates, compacts, briquettes, granules or mixtures of two or more thereof.

12. The method according to claim 10 or claim 11 wherein said method further comprises a latency step between said mixing and said shaping process.

13. The method according to claim 12 wherein said latency step has a duration of at least 18h, preferably of at least 24h.

14. A composition for use as raw material in a steel making process [composition (C), herein after] obtained by the method according to any one of claims 1 to 13 wherein composition (C) after mixing comprises free water in an amount equal to or less than 5.0 wt. %, relative to the total weight of the composition (C).

15. Premix for manufacturing a composition (C) according to any one of claims 9 to 13, wherein said premix comprises said at least one first additive and said at least one second additive.

16. Use of a composition (C) obtained by the method according to any one of claims 1 to 13 as raw material in a steel making process, preferably said steel making process is selected from the group consisting of basic oxygen furnace (BOF) process, electric arc furnace (EAF) process and argon oxygen decarburization process (AOD).

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2024/074346

A. CLASSIFICATION OF SUBJECT MATTER
INV. C21C1/02 C21C7/00 C21C7/06 C21C7/064 C21C7/076
C22B1/244 C22B7/02
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)
C21C C21B C22B

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	US 2003/177864 A1 (NAKAI YOSHIE [JP] ET AL) 25 September 2003 (2003-09-25)	1-14,16
A	paragraph [0094]; claims 20, 29	15

X	EP 0 398 674 A2 (ELKEM METALS [US]) 22 November 1990 (1990-11-22)	1-14,16
A	claims 6,11	15

X	CN 108 486 315 A (UNIV WUHAN SCIENCE & TECH) 4 September 2018 (2018-09-04)	1-14,16
A	claims 1,7; figure 3	15

X	US 2015/344363 A1 (AMIRZADEH-ASL DJAMSCHID [DE]) 3 December 2015 (2015-12-03)	1-14,16
A	paragraphs [0001], [0037], [0047]	15

	-/--	

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"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 13 September 2024	Date of mailing of the international search report 30/09/2024
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 Momeni, Mohammad

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2024/074346

C(Continuation). **DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2017/187973 A1 (UNIV TOHOKU [JP]; HOEI SHOKAI CO LTD [JP]) 2 November 2017 (2017-11-02)	1-14,16
A	claims 1,2,11	15

X	US 2019/144336 A1 (CRINIERE GUILLAUME [BE] ET AL) 16 May 2019 (2019-05-16) paragraphs [0202], [0249]; claim 21	1-16

X	US 4 217 133 A (GOTO TAKESHI [JP] ET AL) 12 August 1980 (1980-08-12) tables I, II, V and VI; examples 1 and 3 column 1; lines 8-13	1-16

X	CN 111 254 257 A (UNIV ANHUI TECHNOLOGY) 9 June 2020 (2020-06-09)	15
A	claim 7	1-14,16

X	EP 0 116 206 A1 (FOSECO INT [GB]) 22 August 1984 (1984-08-22)	15
A	table 3	1-14,16

X	IT 2021 0002 6225 A1 (UNICALCE S P A [IT]) 13 April 2023 (2023-04-13)	15
A	claim 1	1-14,16

X	CN 115 652 027 A (ANGANG STEEL CO LTD) 31 January 2023 (2023-01-31)	15
A	paragraph [0011]	1-14,16

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2024/074346

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2003177864 A1	25-09-2003	AT E328122 T1	15-06-2006
		BR 0111679 A	20-05-2003
		CA 2412666 A1	12-12-2002
		CN 1436250 A	13-08-2003
		DE 60120156 T2	02-11-2006
		EP 1291442 A1	12-03-2003
		JP 4133318 B2	13-08-2008
		KR 20030026246 A	31-03-2003
		TW 558567 B	21-10-2003
		US 2003177864 A1	25-09-2003
		US 2005092133 A1	05-05-2005
		WO 0196616 A1	20-12-2001
EP 0398674 A2	22-11-1990	AT E135748 T1	15-04-1996
		DE 69025981 T2	10-10-1996
		EP 0398674 A2	22-11-1990
		NO 179080 B	22-04-1996
		PL 285228 A1	28-01-1991
		YU 95590 A	20-01-1994
CN 108486315 A	04-09-2018	NONE	
US 2015344363 A1	03-12-2015	BR 112015015692 A2	11-07-2017
		CN 104919061 A	16-09-2015
		DE 102013114865 A1	10-07-2014
		EP 2941489 A1	11-11-2015
		JP 6585747 B2	02-10-2019
		JP 2016510255 A	07-04-2016
		JP 2018090486 A	14-06-2018
		KR 20150103693 A	11-09-2015
		RU 2015132828 A	09-02-2017
		UA 113909 C2	27-03-2017
		US 2015344363 A1	03-12-2015
		WO 2014106506 A1	10-07-2014
WO 2017187973 A1	02-11-2017	CA 3022352 A1	02-11-2017
		EP 3450580 A1	06-03-2019
		JP 6113344 B1	12-04-2017
		JP 2017201054 A	09-11-2017
		KR 20190003577 A	09-01-2019
		TW 201802251 A	16-01-2018
		US 2019106767 A1	11-04-2019
		WO 2017187973 A1	02-11-2017
US 2019144336 A1	16-05-2019	AR 108988 A1	17-10-2018
		AR 108989 A1	17-10-2018
		AU 2017294103 A1	14-02-2019
		AU 2017294107 A1	21-02-2019
		AU 2017294109 A1	21-02-2019
		AU 2017294559 A1	21-02-2019
		AU 2019284111 A1	23-01-2020
		BE 1024901 A1	08-08-2018
		BE 1024902 A1	08-08-2018
		BE 1024903 A1	08-08-2018
		BE 1024907 A1	08-08-2018
		BE 1024908 A1	08-08-2018
		BE 1024910 A1	08-08-2018
		BE 1024911 A1	08-08-2018

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2024/074346

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
		BR 112018075537 A2	19-03-2019
		BR 112018075553 A2	19-03-2019
		BR 112018075560 A2	19-03-2019
		BR 112018075593 A2	26-03-2019
		BR 112018075623 A2	09-04-2019
		CA 3027003 A1	11-01-2018
		CA 3027017 A1	11-01-2018
		CA 3027025 A1	11-01-2018
		CA 3027109 A1	11-01-2018
		CL 2018003655 A1	25-01-2019
		CL 2018003686 A1	01-02-2019
		CL 2019000054 A1	29-03-2019
		CL 2019000055 A1	29-03-2019
		CN 109641756 A	16-04-2019
		CN 109843805 A	04-06-2019
		CN 109982971 A	05-07-2019
		CN 110023243 A	16-07-2019
		EP 3356295 A1	08-08-2018
		EP 3356296 A1	08-08-2018
		EP 3481772 A1	15-05-2019
		EP 3481774 A1	15-05-2019
		EP 3481775 A1	15-05-2019
		ES 2730811 T3	12-11-2019
		ES 2766858 T3	15-06-2020
		ES 2841328 T3	08-07-2021
		FR 3053673 A1	12-01-2018
		FR 3053676 A1	12-01-2018
		FR 3053677 A1	12-01-2018
		FR 3053678 A1	12-01-2018
		FR 3053679 A1	12-01-2018
		FR 3053680 A1	12-01-2018
		FR 3053681 A1	12-01-2018
		JP 6633781 B2	22-01-2020
		JP 6663517 B2	11-03-2020
		JP 6744434 B2	19-08-2020
		JP 2019519686 A	11-07-2019
		JP 2019522111 A	08-08-2019
		JP 2019522112 A	08-08-2019
		JP 2019525880 A	12-09-2019
		JP 2019527176 A	26-09-2019
		JP 2020073437 A	14-05-2020
		KR 20190007010 A	21-01-2019
		KR 20190007012 A	21-01-2019
		KR 20190007014 A	21-01-2019
		KR 20190021233 A	05-03-2019
		KR 20190026664 A	13-03-2019
		PE 20190305 A1	01-03-2019
		PE 20190537 A1	11-04-2019
		PE 20190775 A1	06-06-2019
		PE 20190862 A1	18-06-2019
		PH 12018502566 A1	28-10-2019
		PH 12018502589 A1	30-09-2019
		PH 12018502590 A1	14-10-2019
		PH 12018502591 A1	14-10-2019
		PL 3356295 T3	30-09-2019
		PL 3356296 T3	18-05-2020
		PL 3481774 T3	06-04-2021
		PT 3356295 T	12-06-2019

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
		PT 3356296 T	21-01-2020
		PT 3481774 T	05-01-2021
		SG 11201810909Q A	30-01-2019
		SG 11201810995T A	30-01-2019
		SG 11201811051S A	30-01-2019
		SG 11201811053W A	30-01-2019
		TR 201908317 T4	21-06-2019
		TW 201821366 A	16-06-2018
		TW 201834970 A	01-10-2018
		UA 123366 C2	24-03-2021
		UA 123511 C2	14-04-2021
		UA 123517 C2	14-04-2021
		US 2019144336 A1	16-05-2019
		US 2019292626 A1	26-09-2019
		US 2019337846 A1	07-11-2019
		US 2019337847 A1	07-11-2019
		US 2019345066 A1	14-11-2019
		WO 2018007607 A1	11-01-2018
		WO 2018007629 A1	11-01-2018
		WO 2018007635 A1	11-01-2018
		WO 2018007636 A1	11-01-2018
		WO 2018007637 A1	11-01-2018
		WO 2018007638 A1	11-01-2018
		WO 2018007639 A1	11-01-2018
		ZA 201808204 B	28-10-2020
		ZA 201808206 B	25-03-2020
		ZA 201808210 B	29-07-2020
US 4217133 A	12-08-1980	DE 2911657 A1	11-10-1979
		JP S6058283 B2	19-12-1985
		JP S54125116 A	28-09-1979
		US 4217133 A	12-08-1980
CN 111254257 A	09-06-2020	NONE	
EP 0116206 A1	22-08-1984	AT E22578 T1	15-10-1986
		AU 557070 B2	04-12-1986
		BR 8306781 A	17-07-1984
		CA 1215235 A	16-12-1986
		EP 0116206 A1	22-08-1984
		ES 8600414 A1	01-10-1985
		IN 161305 B	07-11-1987
		JP H0136526 B2	01-08-1989
		JP S59133316 A	31-07-1984
		KR 840007031 A	04-12-1984
		US 4462823 A	31-07-1984
		ZA 838921 B	30-01-1985
IT 202100026225 A1	13-04-2023	EP 4416114 A1	21-08-2024
		WO 2023062430 A1	20-04-2023
CN 115652027 A	31-01-2023	NONE	