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(54) **METHOD FOR MANUFACTURING BRIQUETTES CONTAINING A CALCIUM-MAGNESIUM COMPOUND AND AN IRON-BASED COMPOUND, AND BRIQUETTES OBTAINED THEREBY**

(71) Applicant: **S. A. Lhoist Recherche et Developpement**,
Ottignies-Louvain-la-Neuve (BE)

(72) Inventors: **Guillaume Criniere**, Braine-l'Alleud (BE); **Michael Nispel**,
Louvain-la-Neuve (BE)

(73) Assignee: **S. A. Lhoist Recherche et Developpement**,
Ottignies-Louvain-la-Neuve (BE)

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(57) **ABSTRACT**

Composition in the form of green or thermally treated briquettes comprising at least one "quick" calcium-magnesium compound comprising an iron-based compound and method of production thereof as well uses thereof.

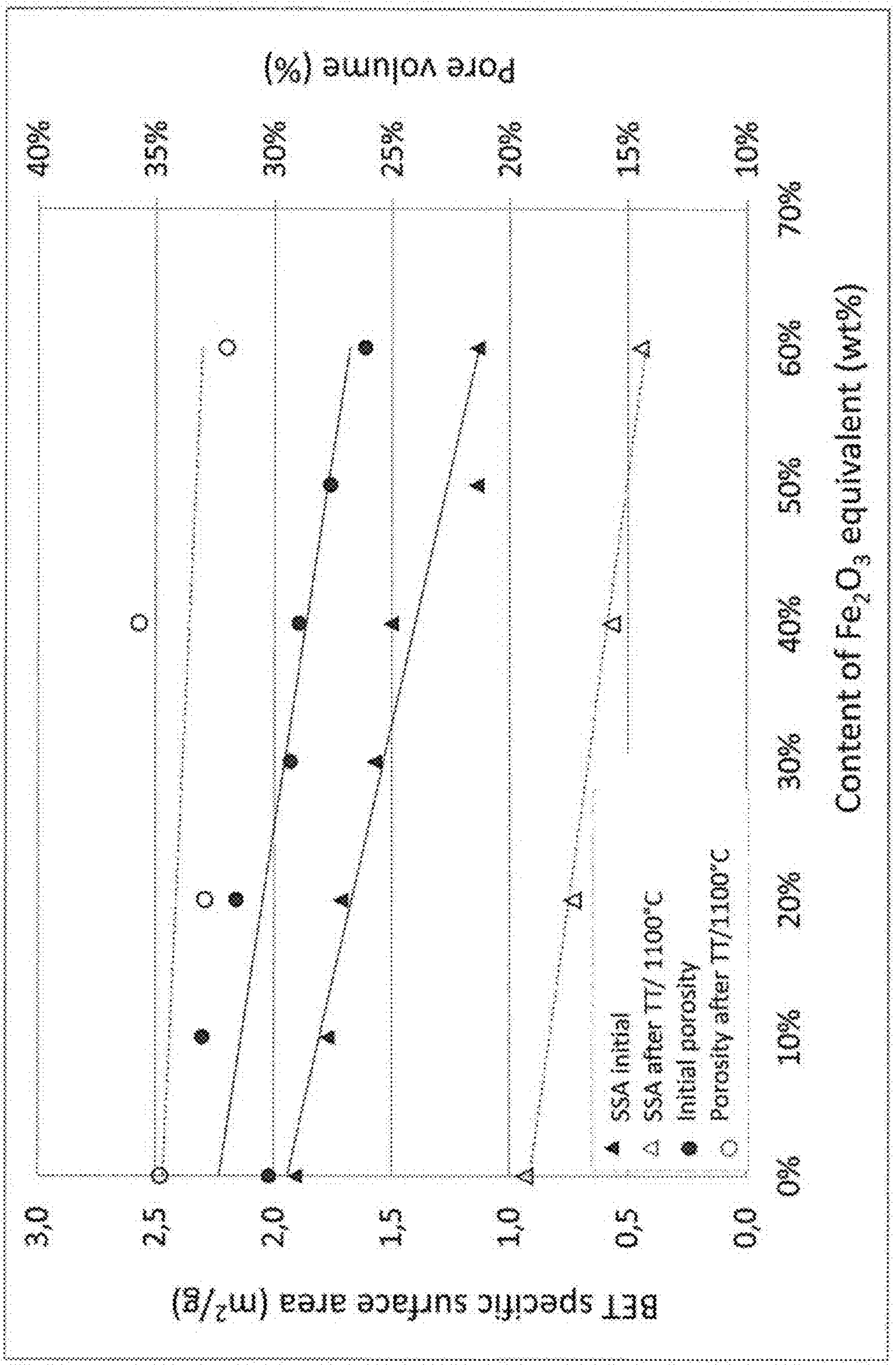
BET specific surface area (m²/g)
3,0
2,5
2,0
1,5
1,0
0,5
0,0
Pore volume (%)
40%
35%
30%
25%
20%
15%
10%
0%
10%
20%
30%
40%
50%
60%
70%
Content of Fe2O3 equivalent (wt%)
▲ SSA initial
△ SSA after TT/ 1100°C
● Initial porosity
○ Porosity after TT/1100°C

Fig. 1

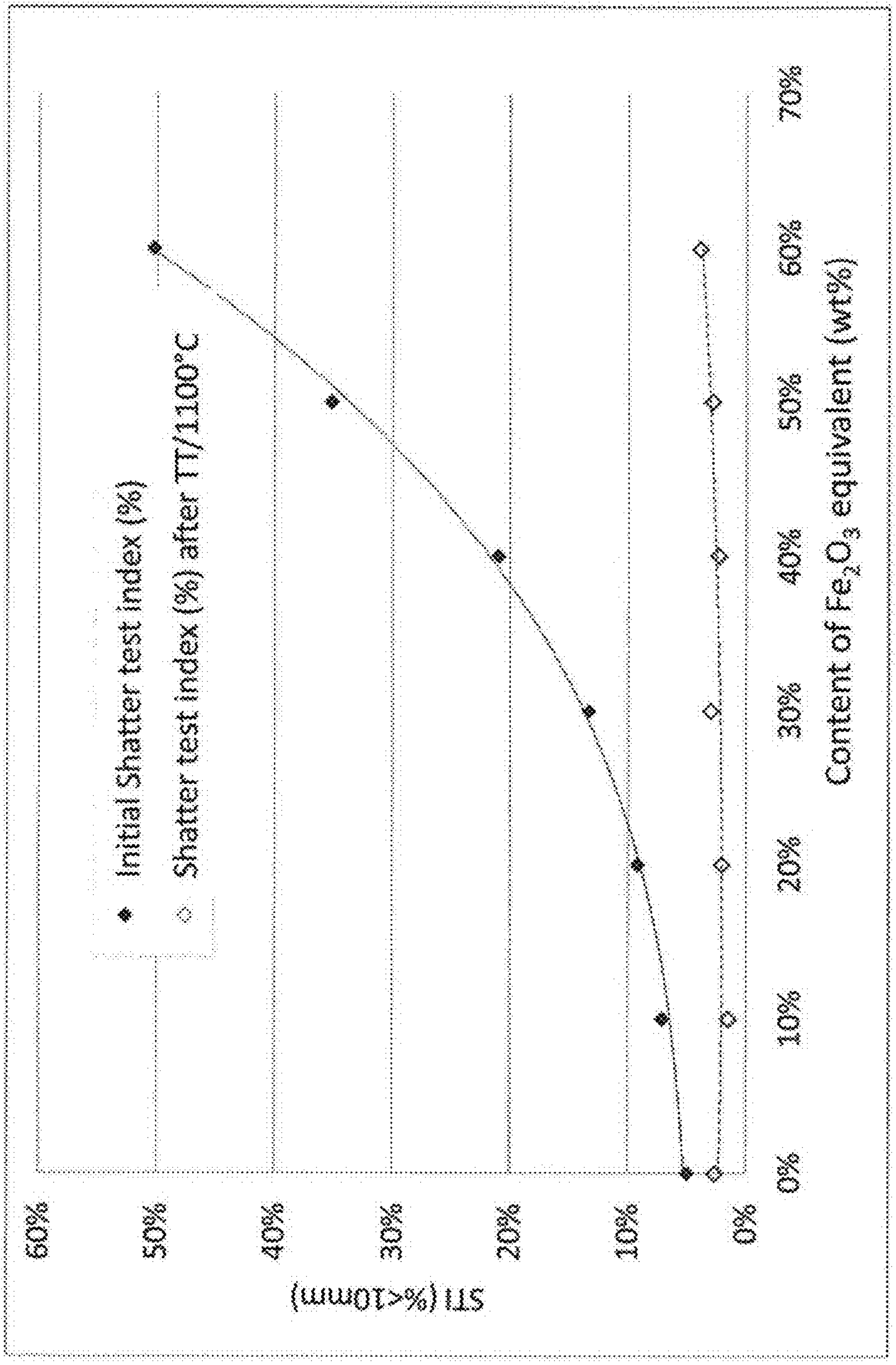
◆ Initial Shatter test index (%)
◇ Shatter test index (%) after TT/1100°C
STI (%<10mm)
60%
50%
40%
30%
20%
10%
0%
0%
10%
20%
30%
40%
50%
60%
70%
Content of Fe_2O_3 equivalent (wt%)

Fig. 2

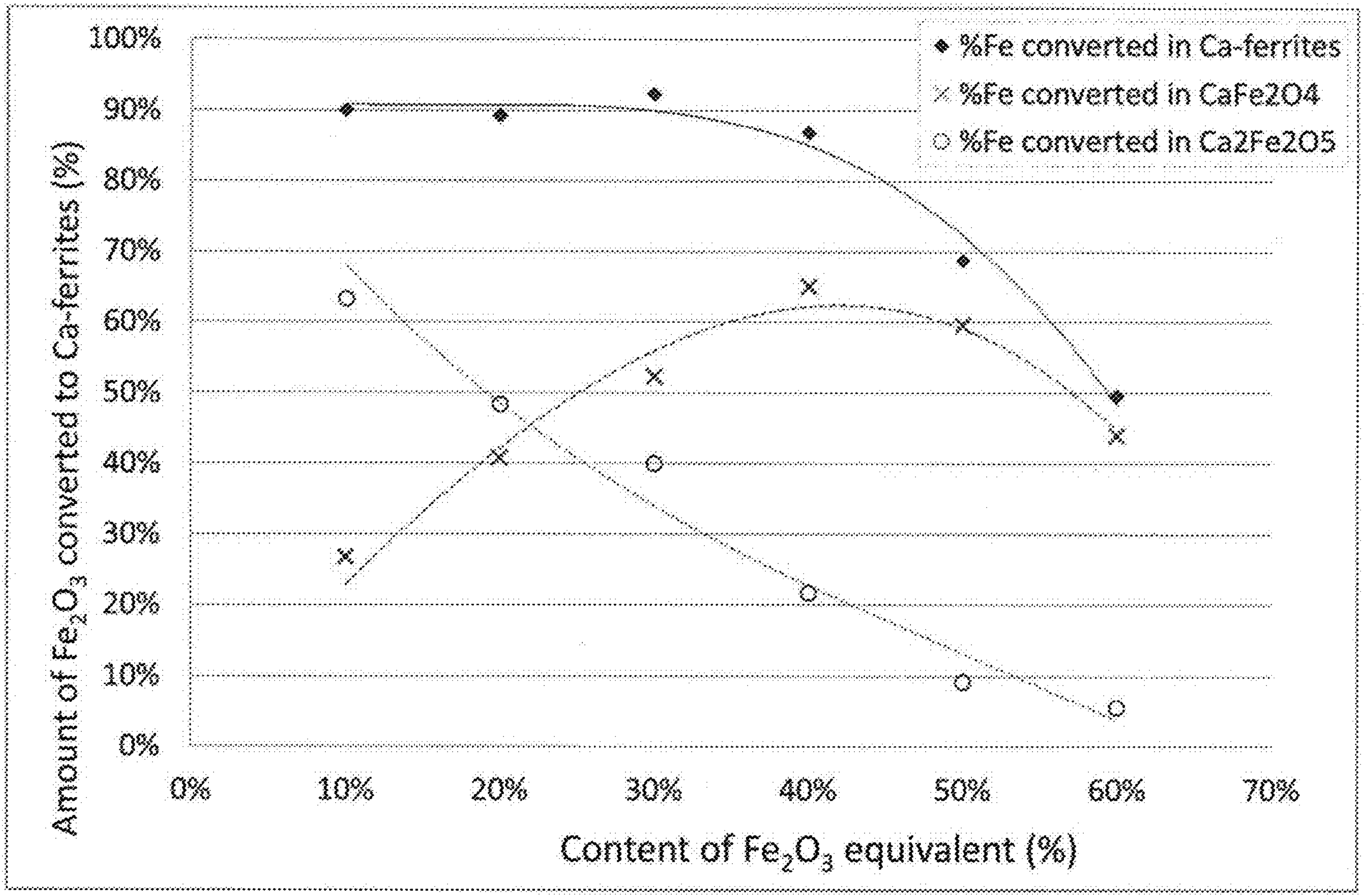
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
Amount of Fe_2O_3 converted to Ca-ferrites (%)
0%
10%
20%
30%
40%
50%
60%
70%
Content of Fe_2O_3 equivalent (%)
◆ %Fe converted in Ca-ferrites
× %Fe converted in CaFe2O4
○ %Fe converted in Ca2Fe2O5

Fig. 3

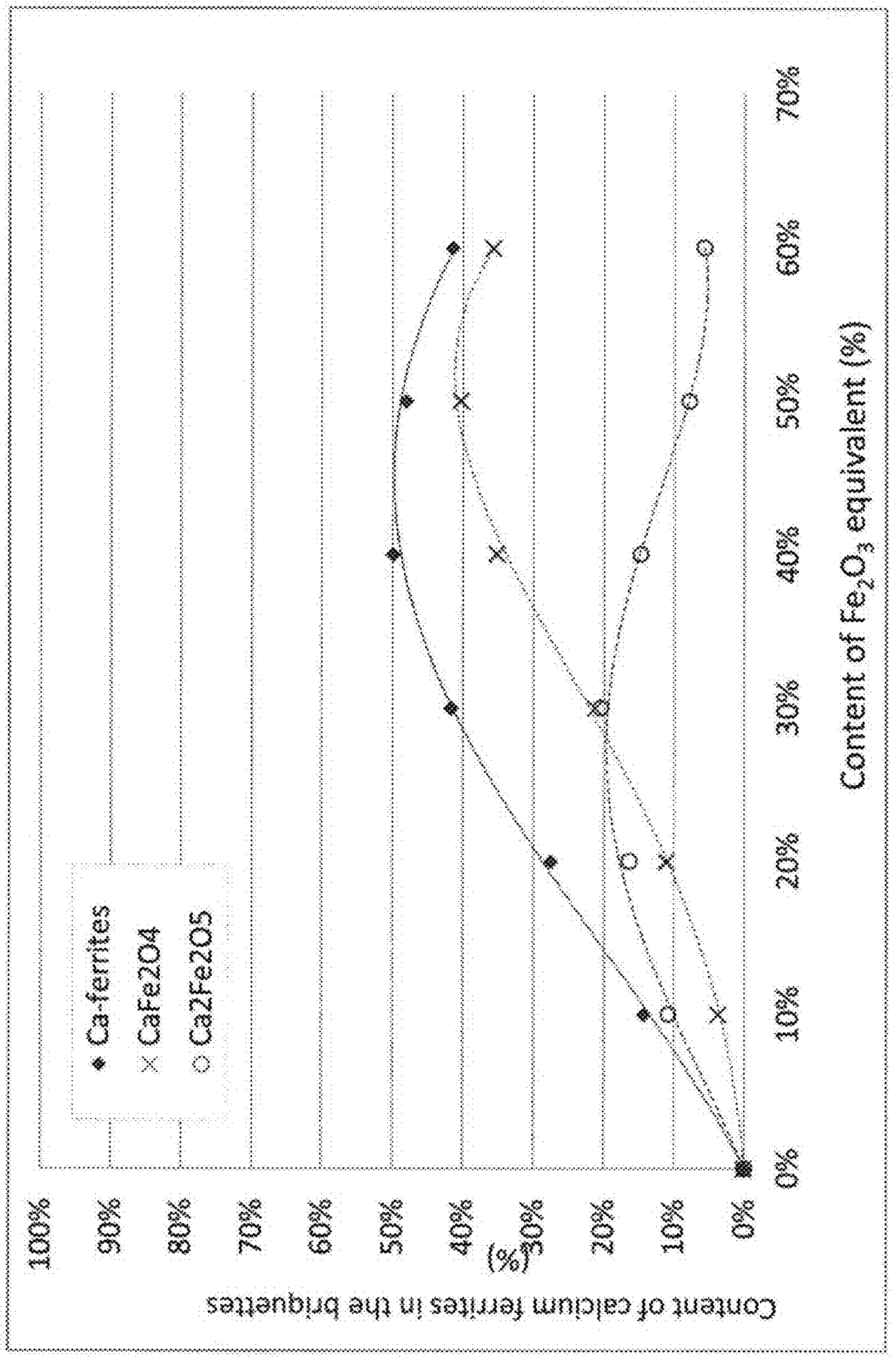
Ca-ferrites
CaFe2O4
Ca2Fe2O5
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
Content of calcium ferrites in the briquettes (%)
0%
10%
20%
30%
40%
50%
60%
70%
Content of Fe$_2$O$_3$ equivalent (%)

Fig. 4

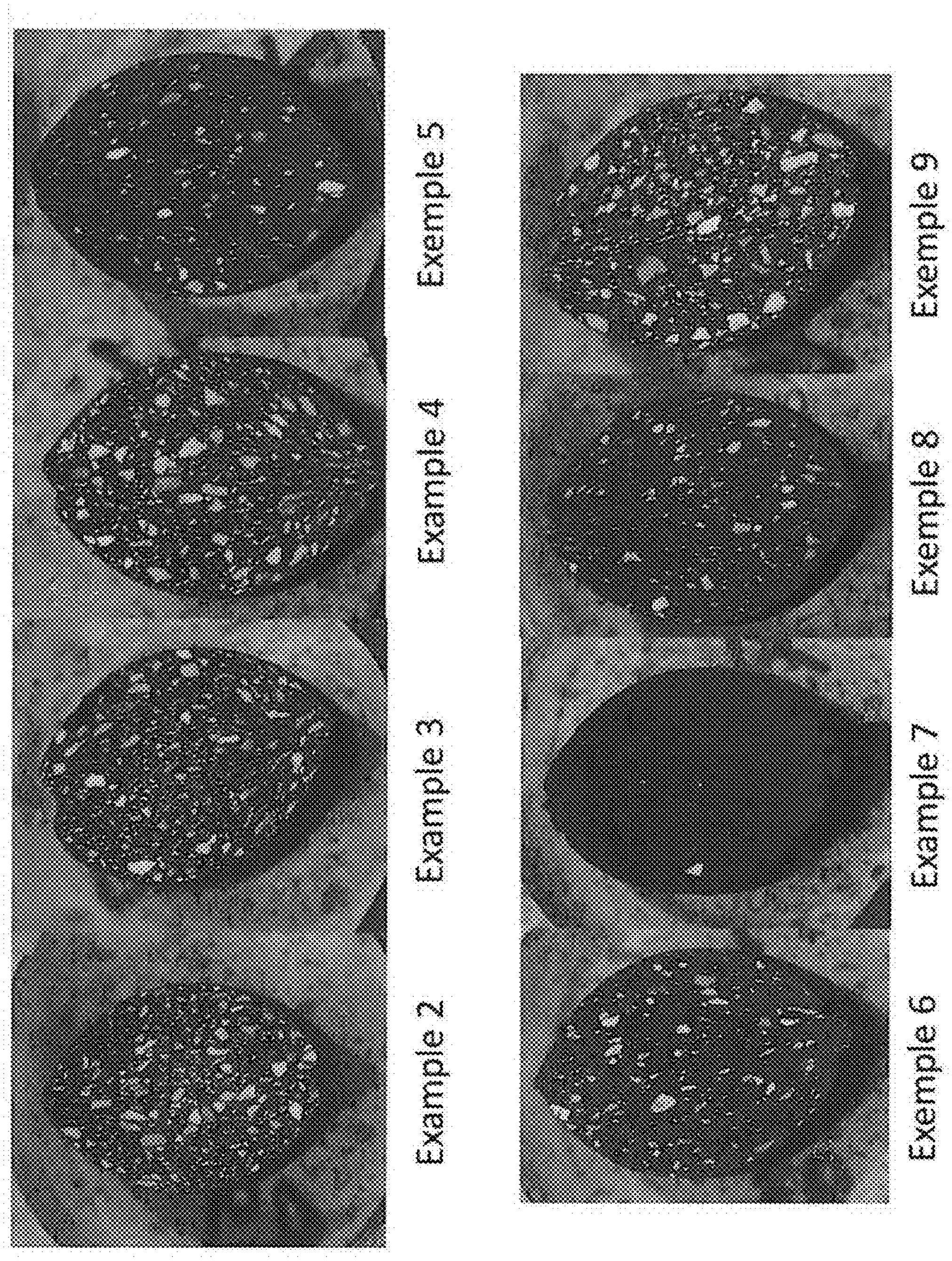
Example 2
Example 3
Example 4
Exemple 5
Exemple 6
Example 7
Exemple 8
Exemple 9

Fig. 5

METHOD FOR MANUFACTURING BRIQUETTES CONTAINING A CALCIUM-MAGNESIUM COMPOUND AND AN IRON-BASED COMPOUND, AND BRIQUETTES OBTAINED THEREBY

[0001] The present invention relates to a method for manufacturing a composition in the form of briquettes containing a “quick” calcium-magnesium compound and an iron-based compound, to green briquettes containing the “quick” calcium-magnesium compound and iron oxide, to thermally treated briquettes containing the “quick” calcium-magnesium compound and calcium ferrites, and to the use thereof.

[0002] The term “quick” calcium-magnesium compound means, in the sense of the present invention, a solid mineral material whose chemical composition is mainly calcium oxide and/or magnesium oxide. The “quick” calcium-magnesium compounds in the sense of the present invention therefore comprise quicklime (calcium lime), magnesium quicklime, dolomitic quicklime or “quick” calcined dolomite. The “quick” calcium-magnesium compounds contain impurities, namely, compounds such as silica, SiO_2 or alumina, Al_2O_3, etc., at the level of a few percent. It is to be understood that these impurities are expressed in the aforementioned forms but may in reality appear as different phases. It also generally contains a few percent of residual $CaCO_3$ or $MgCO_3$, called underburned, and a few percent of residual $Ca(OH)_2$ or $Mg(OH)_2$, owing to partial hydration of the “quick” products during the steps of cooling, handling and/or storage.

[0003] Quicklime means a solid mineral material, whose chemical composition is mainly calcium oxide, CaO. Quicklime is commonly obtained by calcination of limestone, mainly consisting of $CaCO_3$. Quicklime contains impurities, namely compounds such as magnesium oxide MgO, silica SiO_2, or alumina Al_2O_3, etc., at a level of a few percent. It is to be understood that these impurities are expressed in the aforementioned forms but may in reality appear as different phases. It also generally contains a few percent of residual $CaCO_3$, called underburned, and a few percent of residual $Ca(OH)_2$, owing to partial hydration of calcium oxide CaO during the phases of cooling, handling and/or storage.

[0004] According to the present invention, the term “briquette” means a compact of oblong shape, weighing about 5 to 100 g per briquette, inscribed in a flattened or elongated ellipsoid of revolution (“oblate ellipsoid of revolution” or “prolate ellipsoid of revolution”). Typically, briquettes have the shape of a bar of soap or are described as “egg briquettes”.

[0005] These contrast with tablets, which are typically in the form of pellets, such as those produced with the “Titan” presses from the company “Eurotab”. By definition, tablets for industrial use are of regular shape, more particularly in the form of a cylinder with a small height.

[0006] Briquettes are known from the prior art, see for example document WO2015007661. According to this document, compacts (i.e. briquettes or tablets) are described comprising particles of calcium-magnesium compound comprising at least 50% of “quick” calcium-magnesium compound. The compacts (in the form of briquettes or tablets) disclosed may also contain additives, in particular iron oxide.

[0007] According to that document, drop strength (drop mechanical strength) is measured in a Shatter test. The compacts described generally have a Shatter test index below 10%.

[0008] The term “Shatter test index” means, in the sense of the present invention, the percentage by weight of fines under 10 mm generated after 4 drops from 2 m starting from 10 kg of product. These fines are quantified by sieving through a screen with square mesh of 10 mm after 4 drops from 2 m.

[0009] A detailed analysis of the examples and counter-examples of that document shows that green tablets having an improved drop strength were obtained using at least 50% of “quick” products, and that these tablets also display resistance to ageing in humid atmosphere. In contrast, when briquettes of “quick” compounds are obtained using “quick” compounds, the Shatter test index, representing the mechanical strength, remains high (between 13 and 15%) and it is necessary to carry out a thermal treatment if it is desired to reach a Shatter test index below 10%.

[0010] Document U.S. Pat. No. 5,186,742 discloses lime briquettes containing from 55 to 85 wt % of lime, from 10 to 40 wt % of ash and from 0.1 to 10 wt % of paper fibres as well as optionally a lubricant. The briquettes disclosed in document U.S. Pat. No. 5,186,742 were tested for their drop survival rate, a test that is not comparable to the test for measuring the Shatter test index, and they have a crush strength between 150 and 300 pounds, which corresponds to a Shatter test index well above 10%.

[0011] Calcium-magnesium compounds are used in many industries, for example iron and steel metallurgy, treatment of gases, treatment of water and sludge, agriculture, the building industry, public works etc. They may be used either in the form of pebbles or lumps, or in the form of fines (generally smaller than 7 mm). However, the pebble form is preferred in certain industries.

[0012] This is the case, for example, in the iron and steel industry, when adding calcium and magnesium compounds to oxygen converters or arc furnaces.

[0013] During production of these pebbles and lumps, a large number of fines is generated. These fines typically have limited potential for use as they are difficult to transport and handle.

[0014] For some years it has been the aim in a number of sectors to transform compounds initially in the form of powder into briquettes for easier and safer transport, handling and use.

[0015] Lime producers always maintain a balance of materials between the calcium-magnesium compounds in pebble form and the fines generated before and during calcination as well as during handling and subsequent operations. Nevertheless, an excess of fines is produced in certain cases. These fines may then be agglomerated together in the form of briquettes or the like, which not only makes it possible to remove the excess fines but also to increase the production of calcium and magnesium compounds in pebble form artificially by adding these briquettes or the like to the pebbles.

[0016] The document of Barnett et al. (Roll-press briquetting: Compacting fines to reduce waste-handling costs, Powder and Bulk Engineering, Vol. 24, No. 10, October 2010, 1-6) describes a method for manufacturing green lime briquettes. However, this document is silent regarding the production conditions as well as regarding the mechanical properties of the briquettes obtained. Briquettes based on excess fines or the like generally have lower mechanical strength than the calcium and magnesium compounds in pebble form. Their resistance to ageing during storage or handling is also well below that of the calcium and magnesium compounds in pebble form.

[0017] This explains why, in practice, briquetting of fines of calcium and magnesium compounds is not much used at present. Taking into account the low quality of the briquettes formed by this type of process, it is estimated that briquetting provides a yield below 50%, owing to the presence of a very large number of unusable briquettes at the end of this type of process, which requires a recycling step.

[0018] Lubricants and binders are additives that are often used in methods of agglomeration in the form of briquettes or similar.

[0019] Lubricants may be of two types, internal or external. Internal lubricants are mixed intimately with the materials to be briquetted. They promote on the one hand the flowability of the mixture during feed of the briquetting machine and on the other hand rearrangement of the particles within the mixture during compression. External lubricants are applied on the surfaces of the rollers of the briquetting machine and mainly aid mould release. In both cases they reduce friction on the surface and therefore wear. The lubricants may be liquids such as mineral oils, silicones, etc., or solids such as talc, graphite, paraffins, stearates, etc. In the case of compositions based on "quick" calcium-magnesium compounds, stearates are preferred, and more particularly calcium stearate or magnesium stearate.

[0020] Binders are substances having the property of agglomerating the particles together, either by forces of adhesion, or by a chemical reaction. They may be of mineral origin (cements, clays, silicates, etc.), of plant or animal origin (celluloses, starches, gums, alginates, pectin, glues, etc.), of synthetic origin (polymers, waxes, etc.). In many cases they are used together with water, which activates their agglomeration properties.

[0021] Over the years, several of these additives have been used for increasing the strength and durability of the briquettes or similar of calcium and magnesium compounds (calco-magnesian), for example calcium stearate or paper fibres (see for example U.S. Pat. No. 5,186,742), but without this giving sufficient improvement. Moreover, in a great many cases the use of the additives currently employed for other shaped industrial products is limited, as is the case notably for the manufacture of briquettes of calcium-magnesium compounds, either because the calcium-magnesium compounds react violently with water, or owing to a potentially negative effect of these additives on the end use of the briquettes of calcium-magnesium compounds.

[0022] In many refining processes in iron and steel metallurgy, a composition of "quick" calcium-magnesium compounds, such as quicklime and/or "quick" dolomite as well as scrap iron, are added to a converter to control the kinetics and chemistry of the slag forming reaction, thus facilitating removal of impurities and protecting the refractory lining of the furnace against excessive wear.

[0023] The "quick" calcium-magnesium compounds introduced float on the bath of hot metal, thus forming an interface.

[0024] During refining, molten metal is introduced into the vessel, to which scrap iron may also be added.

[0025] The molten metal resulting from the fusion of metal compounds has an initial carbon content typically from 40 to 45 kg per tonne of molten metal and an initial phosphorus content from 0.7 to 1.2 kg per tonne of molten metal.

[0026] The "quick" calcium-magnesium compounds are charged and float above the bath of molten metal. Oxygen is blown in for a predetermined period of time, in order to burn off the carbon and oxidize, directly and/or indirectly, the phosphorus-containing compounds, and silicon. During blowing, the calcium-magnesium compounds are immersed in the bath of molten metal and dissolve/melt slightly at the interface with the molten metal, the calcium-magnesium compounds always floating.

[0027] Slag is the layer of oxides floating on top of the bath and results from the formation of SiO_2 due to oxidation of the silicon, from formation of other oxides (MnO and FeO) during blowing, from addition of "quick" calcium-magnesium compounds for neutralizing the action of SiO_2 on the refractory lining and for liquefying and activating the slag, and from MgO from wear of the refractory lining.

[0028] In fact, during conversion, a metal/gas reaction takes place, in which carbon is burned to form gaseous CO and CO_2. At the end of the predetermined blowing time, the carbon content is reduced to about 0.5 kg per tonne of molten metal, which is about 500 ppm.

[0029] At the interface between the molten metal and the floating calcium-magnesium compounds, a metal/slag reaction takes place, which is intended to remove phosphorus from the molten metal. At the end of the reaction between the slag and the metal, the phosphorus content is about 0.1 kg or less per tonne of molten metal, i.e. about 100 ppm or less.

[0030] If the metal is iron and the calcium-magnesium compound is calcium lime, the chemical reaction is as follows:

$$5\ FeO+4\ CaO+2P \rightleftharpoons 4\ CaO.\ P_2O_5+5\ Fe$$

[0031] The FeO (iron oxide) and the phosphorus are derived from the hot metal, whereas the CaO is added in the converter. This reaction is exothermic and the aim is to shift the equilibrium to the right-hand side. This may be achieved by lowering the temperature, fluidizing the slag as much as possible, homogenizing the metal bath (carried out by blowing argon and/or nitrogen from the bottom in most cases), maintaining the CaO/SiO_2 basicity index between 3 and 6 (the weight ratio of calcium oxide to silica, which is acidic), maintaining the level of magnesite at less than 9% in the slag, and creating sufficient quantities of slag.

[0032] Magnesite is typically present in the slag and is derived from wear of the refractory lining, which may be reduced by controlled addition of "quick" dolomite. However, to favour the kinetics of the reaction in the slag, the level of magnesite should be kept below 9%.

[0033] As will be understood, refining of the hot metal is not so easy, and it would need to be optimized to obtain a given amount of liquid metal, by action on the mass equilibrium of the metal, a given chemical analysis, by action on the mass equilibrium of oxygen (oxidation reaction), and a given temperature at the end of blowing (action on the thermal equilibrium).

[0034] The complexity of improving dephosphorization during refining of hot metal is due, among other things, to simultaneous observation of the three equilibria.

[0035] Such a method for dephosphorization during refining is known in the prior art from the document "Process for dephosphorization of steel in Linz Donawitz converter (BOF converter) by pellet addition" (IN01412MU2006 A).

[0036] This patent focuses on improvement of dephosphorization during a process in a converter by cooling the slag in the second half of the process,

[0037] However, unfortunately the method disclosed requires an additional step in the method for introducing the rocks in the converter after charging the mineral additives and the standard heat-transfer medium. This consequently increases the process time, which is not an acceptable solution for the refining industry, since each second during such a refining process is very expensive.

[0038] Another method for removing phosphorus is known from the document Slag-Making Methods and Materials, patent U.S. Pat. No. 3,771,999. This patent focuses on improving dephosphorization in the method using a converter, by using products based on lime in briquettes having 0.5 to 15% of $CaCl_2$, NaCl, KCl and/or NaF_2.

[0039] Moreover, addition, to lime, of fluxes such as iron oxides, manganese oxides, carbon, CaF_2, and boron oxide, during the refining process, was found in the prior art to improve the quality of the refining process, for example for dephosphorization of molten metal.

[0040] However, addition of such fluxes typically creates additional complexity of the refining process.

[0041] There is therefore a need to supply "quick" calcium-magnesium compounds containing fluxes, in particular iron oxide.

[0042] Briquettes of "quick" calcium-magnesium compounds optionally containing fluxes are known. However, in the known calcium-magnesium compounds containing fluxes, an efflorescence effect has also been reported, which is problematic as blowing then entrains the efflorescence in the fumes (see U.S. Pat. No. 3,649,248). Moreover, it also appeared that when iron oxide is added as flux, it must be converted to ferrite, which then plays a role in acceleration of slag formation.

[0043] However, although this seems simple on paper, the iron oxide converted to ferrite quite often remains negligible, and does not then perform its role in acceleration of slag formation, which leads steelmakers to add lime on the one hand, optionally with iron, and on the other hand ferrite, optionally with lime.

[0044] Formation of calcium ferrites requires relatively high temperatures (typically 1200-1250° C.) and quite long thermal treatment times (see also U.S. Pat. No. 3,649,248). The briquettes based on quicklime (dolomitic) and iron oxide described in the prior art therefore do not lead easily to the formation of calcium ferrites.

[0045] Thus, carrying out said thermal treatment upstream of the converter has an adverse effect from the technical-economic standpoint (specific furnace, energy consumption, loss of production capacity, partial sintering, i.e. reduction of specific surface area and reduction of pore volume).

[0046] When the thermal treatment is carried out in-situ in the converter, the kinetics of formation of calcium ferrites is too slow and has an adverse effect on the performance of these briquettes for dephosphorization.

[0047] Consequently, there is not yet a product that is simple to use, not very restrictive, and that minimizes the loss of lime.

[0048] The present invention aims to solve these drawbacks, at least partly, by supplying a method allowing a considerable reduction in the loss of lime and improvement of the efficacy of the lime in slag formation.

[0049] To solve this problem, a method is provided according to the invention for making a calcium-magnesium composition in the form of briquettes, comprising the following steps:

[0050] i. supplying a pulverulent mixture comprising at least one "quick" calcium-magnesium compound, said mixture comprising at least 40 wt % of CaO+MgO equivalent relative to the weight of said composition and having a Ca/Mg molar ratio greater than or equal to 1, preferably greater than or equal to 2, more particularly greater than or equal to 3 and an iron-based compound having a very fine granulometric distribution characterized by a median size d_{50} below 100 μm, preferably below 50 μm as well as a size d_{90} below 200 μm, preferably below 150 μm, preferably below 130 μm, more preferably below 100 μm;

[0051] ii. feeding a roller press with said homogeneous mixture,

[0052] iii. compressing said pulverulent mixture in said roller press, the rollers of the roller press developing linear speeds at the periphery of the rollers between 10 and 100 cm/s, preferably between 20 and 80 cm/s, and linear pressures between 60 and 160 kN/cm, preferably between 80 and 140 kN/cm, and even more preferably between 80 and 120 kN/cm, obtaining a calcium-magnesium composition in the form of green briquettes, and

[0053] iv. collecting said green briquettes,

wherein said at least one "quick" calcium-magnesium compound comprising at least 40 wt % of CaO+MgO equivalent comprises a fraction of particles of calcium-magnesium compound having a particle size ≤90 μm having at least 20 weight % CaO equivalent with respect to the weight of said pulverulent mixture, and wherein said iron-based compound is present at an amount of at least 20 wt %, preferably at least 25 wt %, more preferably at least 30 wt %, in particular at least 35 wt % relative to the total weight of the pulverulent mixture.

[0054] In a particular embodiment of the invention, said pulverulent mixture comprises at most 97 wt %, preferably at most 90 wt %, preferably at most 88%, in certain embodiments at most 60 wt % of CaO+MgO equivalent relative to the weight of said composition.

[0055] Optionally, in the method according to the present invention, step i. is carried out in the presence of a binder or a lubricant, preferably in the form of powder or concentrated aqueous suspension, more particularly selected from the group consisting of binders of mineral origin such as cements, clays, silicates, binders of vegetable or animal origin, such as celluloses, starches, gums, alginates, pectin, glues, binders of synthetic origin, such as polymers, waxes, liquid lubricants such as mineral oils or silicones, solid lubricants such as talc, graphite, paraffins, stearates, in particular calcium stearate, magnesium stearate and mixtures thereof, preferably calcium stearate and/or magnesium stearate, at a content between 0.1 and 1 wt %, preferably between 0.15 and 0.6 wt %, more preferably between 0.2 and 0.5 wt % relative to the total weight of said briquettes.

[0056] The percentages by weight of CaO+MgO equivalent, but also Fe_2O_3, are determined by X-ray fluorescence spectrometry (XRF) as described in standard EN 15309. Semiquantitative chemical analysis by XRF for determining the relative concentration by weight of the elements whose atomic mass is between 16 (oxygen) and 228 (uranium) is carried out starting from samples ground to 80 μm and formed into pellets. The samples are introduced into PANalytical/MagiX Pro PW2540 apparatus, operating in wavelength dispersion mode. The measurement is performed with a power of 50 kV and 80 mA, with a Duplex detector.

[0057] The analysis results give the calcium, magnesium and iron content and these measurements are reported in weight of CaO and MgO equivalent, and in weight of Fe_2O_3 equivalent.

[0058] According to the present invention, it was in fact found that in contrast to the known compositions, in the briquettes according to the present invention, on the one hand owing to the fact that the mixture formed is homogeneous, but on the other hand also owing to the amount of the iron-based compound present in the form of iron oxide with a very fine particle size distribution, together with the presence of a fraction of particles of calcium-magnesium compound having a particle sizes ≤90 μm in the "quick' calcium-magnesium compound, which latter comprises further at least 20 weight % CaO equivalent with respect to the weight of said pulverulent mixture, a large amount of iron oxide was converted to calcium ferrite, after thermal treatment.

[0059] In addition, when the amount of the iron-based compound, more particularly of iron-based compound with a very fine granulometric distribution is of at least 20 wt % relative to the total weight of the pulverulent mixture, but also the presence of CaO in the calcium-magnesium compound in the form of very fine particles ($d_{30}<90$ μm) is of at least 20 wt %, not only the formation of calcium ferrite is improved and has a yield of conversion of iron oxide to calcium ferrite of about 90%, but also the balance between the formation of monocalcium ferrites and dicalcium ferrites is in favour of forming dicalcium ferrites, particularly when the content of very fine CaO and Fe_2O_3 equivalent is balanced. It has been identified that it can be interesting at an industrial point of view to be able to control the proportion of dicalcium ferrites with respect to the proportion of monocalcium ferrite depending on the needs and vice versa.

[0060] However, although it had been identified in the known compositions that the granulometry of the iron oxide was not adapted, and was often too coarse, the person skilled in the art also knows that the use of fine powders for the calcium-magnesium compound as well as for the iron-based compound, in shaping processes by briquetting runs counter to good practice for a person skilled in the art, since they degrade the flow properties of the mixture and therefore the feeding of the presses.

[0061] The granulometric distribution of the iron-based compound that is used in the method is determined by laser granulometry. Measurement is therefore based on the diffraction of light and follows the theories of Fraunhofer and Mie.

[0062] Notably, it is considered that the particles are spherical, non-porous and opaque. Measurement is carried out according to standard ISO 13320 in methanol, without sonication.

[0063] Moreover, it was demonstrated according to the present invention that it is not only the granulometry that makes it possible to attain a sufficient degree of conversion after thermal treatment or in the converters, but rather that it is necessary for an iron oxide to be available of fine particle size distribution, such as that is active when it is used with the "quick" calcium-magnesium compounds in the form of briquettes.

[0064] The term "iron-based compound", "iron-based compound of very fine particle size distribution" means for example a compound based on iron, preferably based on iron oxide, characterized by a median size d_{50} below 100 μm, preferably 50 μm as well as a size d_{90} below 200 μm, preferably below 150 μm, preferably below 130 μm, more preferably below 100 μm. We may then describe this iron oxide as active iron, which implies in particular that it relative to the total amount of iron oxide present in the iron-based compound, at least 40% of this iron oxide is present in the peripheral layer of the grains of the iron-based compound, said peripheral layer being defined by a thickness of 3 μm. This thus defines a volume fraction of iron oxide at the surface of the iron oxide particles that is able to react, to be converted to ferrite during thermal treatment or else directly in situ in the converter.

[0065] It is also envisaged according to the invention that the iron-based compound is in the form of a mixture of iron-based compounds, wherein said mixture of iron-based compounds may comprise one or more iron oxides, which may in their turn comprise 50 wt %, preferably 60 wt %, preferably 70 wt % of active iron oxide relative to the total weight of said iron-based compound.

[0066] The granulometric distribution of the iron-based compound in the composition in the form of briquettes is determined by scanning electron microscopy and X-ray mapping, coupled to image analysis.

[0067] Measurement is based on the property of the particles of the iron-based compound of emitting X-rays of specific energy (6.398 keV) when they are submitted to high-energy radiation (for example, a high-intensity electron beam). Detection of this radiation, combined with precise knowledge of the position of the electron beam for each point observed, makes it possible to map specifically the particles of the iron-based compound.

[0068] Each particle identified is then characterized by its particle diameter at equivalent surface area ($X_{a,i}$), as defined in standard ISO 13322-1. The particles are then classified by granulometric fraction of particle size.

[0069] In the particular conditions mentioned above, the fraction of active iron in the sense of the invention is in the peripheral layer of each particle of the iron-based compound, in the outer layer with a thickness of 3 μm. For each granulometric fraction and therefore for each particle size, it is therefore possible to calculate the fraction of iron in the peripheral layer from the formula:

$$\%\ Fe_{active/particle}=(V_{ext}-V_{int})/V_{ext}$$

[0070] where V_{ext} is the volume of the particle of the iron-based compound and V_{int} is the volume at the core of the particle at more than 3 μm from the surface, i.e. the volume corresponding to a spherical particle having a radius reduced by 3 μm.

[0071] Considering the particles to be perfectly spherical, the following formula is obtained for the particles whose diameter is greater than 6 μm:

$$\%\ Fe_{active/particle>6\ \mu m}=[(D_{ext})^3-(D_{ext}-6)^3]/(D_{ext})^3$$

[0072] where D_{ext} is the diameter of the particle expressed in μm, or the size of the particle in the sense of laser granulometry.

[0073] The following formula is obtained for the particles whose diameter is under 6 μm:

$$\% \, Fe_{active/particle<6\ \mu m}=100\%$$

[0074] The fraction of total active iron in the sense of the invention is therefore the sum of all the granulometric fractions of the fraction of active iron multiplied by the percentage by volume of each granulometric fraction obtained by laser granulometry

$$\% \, Fe_{active}=\Sigma\%_{volume/particle}\cdot\% \, Fe_{active/particle}$$

[0075] Consequently, to have sufficient active iron oxide in the iron-based compound present in the briquettes produced by the method according to the present invention, the percentage of active iron must be at least 40%.

[0076] As can be seen, according to the present invention, it is not sufficient to have a fine granulometry, it is in fact necessary to attain the percentage of active iron oxide in the iron-based compound present in the briquettes, which makes it possible to attain sufficient conversion to ferrite during preliminary thermal treatment or in a converter.

[0077] Moreover, in the method according to the present invention, it was found that said active iron oxide did not have an adverse effect on the mechanical strength of the briquettes formed, even at a high content of 60 wt % relative to the total weight of the green briquettes.

[0078] Furthermore, formation of these green briquettes with a high content of iron oxide gives briquettes supplying simultaneously fluxes such as iron oxide (Fe_2O_3), but also the required ferrites, because even if the green briquettes do not contain ferrites directly, the ferrites can be formed directly in situ, for example in the converters in which the briquettes are used.

[0079] The method according to the present invention therefore makes it possible to obtain briquettes of calcium-magnesium compounds whose mechanical strength is not mandatorily impaired by adding fluxes, even without thermal treatment for contents of iron oxide below 40 wt % of the composition of the green briquette, in which the iron oxide has a very fine granulometric distribution characterized by a median size d_{50} below 100 μm, preferably below 50 μm as well as a size d_{90} below 200 μm, preferably below 150 μm, preferably below 130 μm, more preferably below 100 μm, and which moreover is very flexible and has good performance, without the aforesaid constraints.

[0080] In the sense of the present invention, said iron-based compound may be formed from one or more iron-based compounds, together totalling a content in the composition of at least 3 wt %, preferably at least 12 wt %, more preferably at least 20 wt %, preferably at least 25 wt %, preferably at least 30 wt %, more preferably at least 35 wt %.

[0081] In another preferred embodiment according to the invention, said iron-based compound has a granulometric distribution characterized by a d_{50} less than or equal to 80 μm, preferably less than or equal to 60 μm.

[0082] In the sense of the present invention, unless stated otherwise, the notation d_x represents a diameter expressed in μm, measured by laser granulometry in methanol without sonication, relative to which x vol % of the particles measured are less than or equal.

[0083] In the case of "quick" calcium-magnesium compound, in particular of quicklime, the measure method of particle size distribution is done by sieving and not by laser diffraction.

[0084] In a particular embodiment, the method according to the present invention further comprises thermal treatment of the green briquettes at a temperature comprised between 900° C. and 1200° C., preferably comprised between 1050° C. and 1200° C. included, more preferably between 1100° C. and 1200° C. included.

[0085] The thermal treatment is carried out preferably for a predetermined time between 3 and 20 minutes, preferably greater than or equal to 5 minutes and less than or equal to 15 minutes, with formation and production of thermally treated briquettes, in which said iron oxide has been converted to calcium ferrite, in particular under the form of monocalcium ferrites, i.e. thermally treated briquettes comprising a "quick" calcium-magnesium compound and an iron-based compound comprising at least calcium ferrite, the iron-based compound comprising at least calcium ferrite, which is present at a content of at least 3%, preferably at least 12%, more preferably at least 20%, preferably at least 30%, more preferably at least 35% in Fe_2O_3 equivalent.

[0086] When the thermal treatment is carried out in "multilayer" conditions, i.e. when the briquettes are in the form of a static bed of briquettes of a certain thickness, it will be understood that the thermal treatment time can be increased to allow time for the heat to penetrate to the centre of the bed of briquettes. In conditions with temperatures less than or equal to 1200° C., thermal treatment makes it possible to obtain thermally treated briquettes comprising a calcium-magnesium compound and an iron-based compound containing calcium ferrite, with little or no change in its porosity and specific surface area, and whose mechanical strength has been improved. In other words, the phenomenon of sintering of the briquettes is avoided at these temperatures. These relatively high porosity characteristics allow rapid dissolution of the thermally treated briquettes in the slag in a metallurgical refining process.

[0087] Thus, it was observed that briquettes obtained by the method according to the present invention not only have a sufficiently high content of calcium ferrite, but the briquettes have particularly interesting mechanical strength represented by the Shatter test index.

[0088] In addition, during thermal treatment, when the composition in the form of green briquettes comprises said "quick" calcium-magnesium compound comprising at least a fraction of particles of calcium-magnesium compound having a particle size ≤ 90 μm, which latter comprises at least 20 wt % CaO equivalent relative to the weight of the pulverulent mixture as well as the iron-based compound present at an amount of at least 20 wt %, preferably at least 25 wt %, more preferably at least 30 wt %, in particular at least 35 wt % relative to the total weight of the pulverulent mixture, a calcium ferrite matrix is formed.

[0089] Said matrix is to be understood as being a continuous phase based on calcium ferrite, in which particles of "quick" calcium-magnesium compound, in particular quicklime, are dispersed. A distinction is made between the case when said particles of "quick" calcium-magnesium compound are of small size, so that they melt visibly in the matrix based on calcium ferrite, and the case when particles of "quick" calcium-magnesium compound are of larger size, appearing as inclusions of "quick" calcium-magnesium compound in said matrix.

[0090] The aforesaid distinction is made concrete on the basis of a section of a briquette according to the invention, applying scanning electron microscopy coupled to energy dispersive analysis. This provides visualization in two dimensions (the surface of the section) of an object initially in three dimensions (briquette), but also of the particles that make up the briquette. Thus, the particles of calcium-magnesium compound also appear in two dimensions on the section plane. As it is customary to liken particles in three dimensions to spheres and determine their size as the diameter of the equivalent sphere ("three-dimensional" size), in the present invention the cut surface of the particle is likened to an equivalent disk and its "two-dimensional" size to the equivalent diameter of this disk. More precisely, the two-dimensional sizes are calculated with a program that finds, for each particle of "quick" calcium-magnesium compound dispersed in the continuous matrix of calcium ferrite, the sum of the smallest and the largest dimension of its cut surface divided by two. This sum divided by two represents the diameter of the equivalent disk.

[0091] in this acceptation, it is considered that the particles of "quick" calcium-magnesium compound melt or merge in said matrix (continuous phase) of calcium ferrite when said particles of "quick" calcium-magnesium compound have a two-dimensional size under 63 μm, observable by scanning electron microscopy coupled to energy dispersive analysis, in a section of the briquette.

[0092] In fact, in certain embodiments of the method according to the present invention, the thermally treated briquettes have a Shatter test index below 8%, sometimes below 6%, below 4%, below 3%, or even around 2%.

[0093] This means that according to the present invention, we have been able to produce very strong briquettes, whose loss due to broken briquettes or to the formation of fines during transport is reduced significantly and it is possible to overcome the drawbacks of the known briquettes, which quite often generate a loss even exceeding 20% of quicklime owing to the generation of fines during transport to the steelmaking shop and owing to handling and transport within the steelmaking shop.

[0094] In yet another particularly advantageous embodiment, said "quick" calcium-magnesium compound is a soft- or medium-burned calcium-magnesium compound, preferably soft-burned.

[0095] In fact, in the method according to the present invention, it is advantageous if the calcium-magnesium compound supplied in the form of a homogeneous mixture is itself also sufficiently reactive, so as to form cohesive briquettes with the iron-based compound after thermal treatment. Moreover, for use in converters for forming slag, it is advantageous for the "quick" calcium-magnesium compound to be sufficiently reactive.

[0096] The "quick" calcium-magnesium compounds, like quicklime, are produced industrially by baking natural limestones in various types of kilns, such as shaft kilns (dual-flow regenerative kilns, annular kilns, standard shaft kilns, etc.) or else rotary kilns. The quality of the calcium-magnesium compound, such as quicklime for example, notably its reactivity with water, and the consistency of this quality, are partly linked to the type of kiln used, the operating conditions of the kiln, the nature of the limestone from which the "quick" calcium-magnesium compound is derived per se, or else the nature and the amount of fuel used. Thus, it is theoretically possible to produce a whole range of "quick" calcium-magnesium compounds, for example quicklime with reactivities with water ranging from the most explosive to the slowest.

[0097] Advantageously, said "quick" calcium-magnesium compound is quicklime.

[0098] In general, production of quicklime by mild baking (900-1000° C.) makes it possible to obtain rather reactive lime, whereas production of lime of low reactivity involves overburning at higher temperature (1200-1400° C.). Overburning quite often leads to the production of quicklime of less stable quality in terms of reactivity with water as the calcining operation is carried out in a thermal zone where the textural development of the quicklime is fairly sensitive. This overburned quicklime is moreover more expensive to produce than a milder quicklime as it requires the use of higher temperatures, but also because, unless dedicated kilns are used, production of this overburned quicklime leads to pauses in production campaigns to alternate with the production of mild quicklimes, which are more commonly used, which is not without problems in stabilization of the calcination conditions and therefore problems in stabilization of quality.

[0099] Quicklimes obtained by mild baking generally have specific surface areas measured by nitrogen adsorption manometry after vacuum degassing at 190° C. for at least 2 hours, calculated by the multiple-point BET method as described in standard ISO 9277:2010E, above 1 m^2/g whereas the overburned quicklimes generally have surface areas well below 1 m^2/g.

[0100] In the context of this invention, the reactivity of quicklime is measured using the water reactivity test of European standard EN 459-2:2010 E. Thus, 150 g of quicklime is added with stirring to a cylindrical Dewar of 1.7 dm^3 capacity containing 600 cm^3 of deionized water at 20° C. The quicklime is supplied in the form of fines with a size between 0 and 1 mm. Stirring at 250 revolutions per minute is carried out with a specific paddle. The temperature variation is measured as a function of time, making it possible to plot a curve of reactivity. The value of t_{60}, which is the time taken to reach 60° C., can be found from this curve.

[0101] The reactivity of burned dolomite is measured using this same reactivity test. In this case, 120 g of burned dolomite is added with stirring to a cylindrical Dewar of 1.7 dm^3 capacity containing 400 cm^3 of deionized water at 40° C. The burned dolomite is supplied in the form of fines with a size between 0 and 1 mm. Stirring at 250 revolutions per minute is carried out by means of a specific paddle. The temperature variation is measured as a function of time, making it possible to plot a curve of reactivity. The value of t_{70}, which is the time taken to reach 70° C., can be found from this curve.

[0102] The composition according to the present invention comprises a soft- or medium-burned calcium-magnesium compound, preferably soft-burned, which is therefore necessarily relatively reactive, thus supplying reactive briquettes.

[0103] According to the present invention, a soft- or medium-burned calcium-magnesium compound, preferably soft-burned, is characterized by a value of t_{60} below 10 min, preferably 8 min, preferably 6 min, and more preferably 4 min when the calcium-magnesium compound is a quicklime and by a value of t_{70} below 10 min, preferably 8 min, preferably 6 min, and more preferably 4 min when the calcium-magnesium compound is a burned dolomite.

[0104] In a particular embodiment of the method according to the present invention, the method comprises, before said supplying of a pulverulent mixture:

[0105] i. feeding a mixer with at least 40 wt % of CaO+MgO equivalent from "quick" calcium-magnesium compound relative to the weight of said composition and with at least 20 wt %, preferably at least 25 wt %, more preferably at least 30 wt %, more preferably at least 35 wt % of Fe_2O_3 equivalent from an iron-based compound relative to the weight of said composition, said iron-based compound having a very fine granulometric distribution characterized by a median size d_{50} below 100 μm, preferably below 50 μm as well as a size d_{90} below 200 μm, preferably below 150 μm, preferably below 130 μm, more preferably below 100 μm; said "quick" calcium-magnesium compound comprising at least 40 wt % CaO+MgO equivalent comprises also at least a fraction of particles of calcium-magnesium compound having a particle size ≤90 μm, which latter comprises further 20 wt % CaO equivalent relative to the weight of the pulverulent mixture, and,

[0106] ii. mixing said "quick" calcium-magnesium compound with said iron-based compound for a predetermined length of time, sufficient to obtain an approximately homogeneous pulverulent mixture of said "quick" calcium-magnesium compound and of said iron-based compound.

[0107] Advantageously, according to the present invention, said fraction of particles of calcium-magnesium compound present a particle size ≤90 μm, which latter comprises at most 60 wt % equivalent CaO with respect to the weight of the pulverulent mixture.

[0108] More particularly, in the method according to the present invention, although a binder or lubricant may be added directly at the level of feeding the roller press, said binder or lubricant is added to the mixer, wherein said binder or lubricant is included in said pulverulent mixture, preferably homogeneous.

[0109] In another particular embodiment of the method according to the present invention, said calcium-magnesium compound contains at least 10 wt % of quicklime in the form of ground particles relative to the weight of said composition.

[0110] Advantageously, said calcium-magnesium compound according to the present invention contains at least 40 wt %, preferably at least 50 wt %, preferably at least 60 wt %, particularly at least 65 wt %, in particular at least 70 wt %, preferably at least 80 wt %, advantageously at least 90 wt %, or even 100 wt % of quicklime in the form of ground particles relative to the weight of said composition.

[0111] "Quicklime in the form of ground particles" refers to the lime fines resulting from grinding quicklime and therefore corresponding to a size reduction of the limestone. Grinding may be carried out either starting from the ungraded material leaving the furnace and/or leaving the storage bin or starting from the ungraded material leaving the furnace and/or leaving the storage bin, screened beforehand. Grinding may be carried out using different types of grinding mills (impact crusher, hammer crusher, double roll crusher, cone crusher, etc.), either in open circuit (no recycling loop), or in closed circuit (recycling loop).

[0112] Quicklime in the form of ground particles (also called ground lime) differs from screened lime. Screened lime means the lime fines resulting from screening of lime. The granulometry is defined by the size of the screen. For example, a lime screened at 3 mm gives a 0-3 mm screened lime. Thus, screening of the ungraded material leaving the furnace leads to a "primary" screened lime. Screening of the ungraded material leaving the storage bin leads to a "secondary" screened lime.

[0113] In the sense of the present invention, quicklime in the form of ground particles means lime fines generally containing more very fine particles than the lime fines from screening. Thus, if we consider for example 0-3 mm fines, quicklime fines in the form of ground particles will typically contain at least 30 wt %, most often at least 40 wt %, or even at least 50 wt % of very fine particles under 100 μm, whereas screened lime fines will often contain at most 25 wt %, or even at most 15 wt % of very fine particles under 100 μm.

[0114] The chemical composition of the fines of ground lime is generally more uniform than that of the screened lime fines. Thus, if we consider for example a 10-50 mm limestone calcined with an ash-generating fuel such as coal (lignite, hard coal, anthracite, etc.) or else petroleum coke, and characterize the 0-3 mm fines resulting from grinding or screening of this limestone, it will be found that the 0-200 μm fraction of the 0-3 mm fines resulting from grinding has a similar chemistry to that of the 200 μm-3 mm fraction, whereas the 0-200 μm fraction of the 0-3 mm fines resulting from screening contains more impurities than the 200 μm-3 mm fraction.

[0115] The fines of ground lime are in general more reactive than the screened lime fines. Thus, for soft-burned quicklime, if we measure the reactivity with water (standard EN459) of the 0-3 mm fines, the fines from grinding typically have values of t_{60} below 5 min whereas the fines from primary screening often have values of t_{60} above 5 min.

[0116] In fact it was found, surprisingly, without it being possible at present to explain why, that addition of quicklime in the form of ground particles at a concentration of at least 10 wt % relative to the weight of the briquettes made it possible to obtain a greatly improved drop strength. A content as limited as 10 wt % makes it possible to obtain a significant improvement in mechanical strength, although the content of ground particles may be up to 100 wt %.

[0117] More particularly, said quicklime in the form of ground particles is a soft-burned or medium-burned quicklime, preferably soft-burned, said quicklime in the form of ground particles being characterized by a value of t_{60} below 10 min, preferably below 8 min, preferably below 6 min, and more preferably below 4 min.

[0118] In a preferred embodiment of the method according to the present invention, the method further comprises a pre-treatment step of the briquettes under modified atmosphere containing at least 2 vol % CO_2 and at most 30 vol % CO_2, preferably at most 25 vol % CO_2, preferably at most 20 vol % CO_2, more preferably at most 15 vol % CO_2, even more preferably at most 10 vol % CO_2 with respect to the modified atmosphere.

[0119] It has been indeed identified according to the present invention that a pre-treatment under such modified atmosphere containing such CO_2% with respect to the modified atmosphere allows to increase the mechanical strength of the briquettes.

[0120] In an advantageous variation of the present invention, said pulverulent mixture comprises less than 10% of particles of "quick" calcium-magnesium compound having a particle size ≥90 μm and ≤5 mm relative to the total weight of the pulverulent mixture.

[0121] Due to this, the briquettes obtained by the method according to the present invention, have a relative particle size homogeneity, i.e. that when the briquette is cut, it has a granular composition in the major fraction of its volume. One can therefore observe a continuous phase, made by calcium ferrite, by calcium-magnesium compound, such as for example of quicklime and optionally of iron-based compound, such as iron oxide, depending on the initial content in the green briquette of calcium-magnesium compound, of calcic component in this latter, of iron-based compound.

[0122] In this acceptation, it is considered that the particles of "quick" calcium-magnesium compound melt or merge in said matrix (continuous phase) of calcium ferrite when said particles of "quick" calcium-magnesium compound have a two-dimensional size under 63 μm, observable by scanning electron microscopy coupled to energy dispersive analysis, in a section of the briquette.

[0123] It is considered, moreover, that inclusions of "quick" calcium-magnesium compound are present in the matrix based on calcium ferrite, when particles of "quick" calcium-magnesium compound having a two-dimensional size above 63 μm, observable by scanning electron microscopy coupled to energy dispersive analysis in a section of the briquette, cover at least 20% of the area of said section.

[0124] It is also considered that if particles of "quick" calcium-magnesium compound having a two-dimensional size above 63 μm, observable by scanning electron microscopy coupled to energy dispersive analysis, are present in a section of the briquette but cover less than 20%, in particular less than 10% of the surface area of said section, true inclusions of "quick" calcium-magnesium compounds are not present, but rather some particles of "quick" calcium-magnesium compounds are present by chance, notably resulting from the imperfect nature of the manufacturing process, in particular the thermal treatment, of the briquette.

[0125] Briquettes of calcium ferrites without significant presence of inclusions of "quick" calcium-magnesium compounds are therefore usable in iron and steel metallurgy, notably in a converter for refining molten metal, to facilitate slag formation. Such briquettes therefore clearly offer an advantage in accelerating the formation of slag and increasing its fluidity.

[0126] However, calcium ferrites themselves do not allow refining of molten metal, namely trapping its impurities. It is only the calcium-magnesium compound, in particular quicklime, that can provide this function. It is therefore possible to add for example quicklime as lumps or briquettes of quicklime simultaneously with the briquettes based on calcium ferrites according to the invention.

[0127] In another advantageous variation of the present invention, said pulverulent mixture comprises between 10 and 60% of particles of "quick" calcium-magnesium compound having a particle size ≥90 μm and ≤5 mm relative to the total weight of the pulverulent mixture.

[0128] An advantageous alternative according to the invention is to provide inclusions of "quick" calcium-magnesium compounds, in particular of quicklime, dispersed in the continuous phase (matrix) of calcium ferrite, as described above. In fact, the "quick" calcium-magnesium compound is then available in situ at the place where the calcium ferrites have promoted slag formation, acting as flux to allow the "quick" calcium-magnesium compound to act immediately.

[0129] In this advantageous variation of the method, it has been identified upon cutting the thermally treated briquette according to the present invention, the section plane contains spread inclusions of calcium-magnesium compound and/or quicklime, which allows to have those latter under the form of quicklime having not reacted to form calcium ferrites under quicklime and which are still available for a use under the form of quicklime, such as for example in the steelmaking, such as for slag formation. The content of those inclusions of calcium-magnesium compound can be more or less important such as explained here above in the section related to thermally treated briquettes according to the present invention.

[0130] More particularly, in the method according to the present invention, said at least one iron-based compound is present at an amount higher or equal to 20 wt %, preferably of at least 25 wt %, more preferably of at least 30 wt %, in particular of at least 35 wt % relative to the total weight of the pulverulent mixture.

[0131] When the content of iron-based compound, more particularly of iron oxide of very fine particle size distribution is at least 20 wt % relative to the weight of the pulverulent mixture, but also when the presence of CaO in the calcium-magnesium compound under the form of very fine particles (d_{30}<90 μm) is at least 20 wt %, not only the calcium ferrite formation is improved and has a conversion yield of iron oxide to calcium ferrite of about 90%, but also the balance between monocalcium ferrites and dicalcium ferrites is in favour of dicalcium ferrite, in particular when the amount in CaO and Fe_2O_3 equivalent are balanced. It has been indeed identified that it can be interesting to be able to control the ratio of dicalcium ferrites with respect to the one of monocalcium ferrites depending on the needs and inversely.

[0132] In a preferred embodiment of the method according to the present invention, the wt % of CaO equivalent in the fraction of "quick" calcium-magnesium compound having a particle size <90 μm with respect to the total of the wt % of quicklime in the fraction of calco-magnesium compound having a particle size <90 μm and the % Fe_2O_3 equivalent of the iron-based compound having a very fine particle size distribution is ≥30%, preferably ≥32%, preferably ≥34%, in a particularly preferred manner ≥36%.

[0133] In a preferred embodiment of the method according to the present invention, the wt % of CaO equivalent in the fraction of "quick" calcium-magnesium compound having a particle size <90 μm with respect to the total of the wt % of quicklime in the fraction of calco-magnesium compound having a particle size <90 μm and the % Fe_2O_3 equivalent of the iron-based compound having a very fine particle size distribution is <40, preferably <38, more preferably <36% %, and higher than 20%, preferably higher than 22%, preferably 24%.

[0134] In fact it was found, advantageously, that it was possible to influence and control the proportion of monocalcium ferrite and dicalcium ferrite during thermal treatment of the briquettes by adjusting the percentage by weight of said quicklime particles having a particle size <90 μm relative to the total of the percentage by weight of said quicklime particles.

[0135] When the percentage by weight of CaO equivalent in the fraction of "quick" calcium-magnesium compound having a particle size <90 μm relative to the total of the percentage by weight of quicklime in the fraction of calcium-magnesium compound having a particle size <90 μm and the percentage of Fe_2O_3 equivalent of said iron-based compound with very fine granulometric distribution is ≥20%, preferably ≥30%, more preferably ≥35% and in a particularly preferred manner, ≥40%, thermal treatment of the briquettes will rather promote the formation of dicalcium ferrite ($Ca_2Fe_2O_5$).

[0136] This means that if:

[0137] P1 represents the percentage, in the pulverulent mixture intended for briquetting, of the particles of the "quick" calcium-magnesium compound whose size is under 90 μm (fraction of calcium-magnesium compound having a particle size <90 μm),

[0138] P2 represents the percentage, in the pulverulent mixture intended for briquetting, of the particles of the "quick" calcium-magnesium compound whose size is above 90 μm,

[0139] P3: percentage of the iron-based compound (with very fine granulometric distribution) in the pulverulent mixture intended for briquetting,

[0140] C1 represents the percentage of CaO equivalent in the particles of "quick" calcium-magnesium compound whose size is under 90 μm

[0141] C2 represents the percentage of CaO equivalent in the particles of "quick" calcium-magnesium compound whose size is above 90 μm

[0142] C3 represents the percentage of Fe_2O_3 equivalent in the iron-based compound

[0143] The weight ratio "P1/(P1+P3)" is a key parameter that must be controlled for forming either predominantly monocalcium ferrites or predominantly dicalcium ferrites, and more generally the weight ratio "P1.C1/(P1.C1+P3.C3)" is one of the possibilities for predominant formation of monocalcium ferrite or else predominant formation of dicalcium ferrite.

[0144] In such a case said thermal treatment is preferably a thermal treatment with a temperature higher than or equal to 1100° C., preferably higher than or equal to 1150° C., more particularly less than or equal to 1200° C., preferably according to the relationship (predefined period)/(temperature of thermal treatment−1000° C.)>5.

[0145] The percentage P2 is a key parameter that must be controlled for forming briquettes with or without inclusions of "quick" calcium-magnesium compound having a two-dimensional size above 63 μm.

[0146] In another preferred embodiment, the iron-based compound comprises at least 50 wt %, preferably at least 60 wt %, more preferably at least 70 wt %, more preferably at least 80 wt % and in a particular manner more than 95 wt % iron oxide under the form of magnetite Fe_3O_4 relative to the total weight of the iron based compound expressed in Fe_2O_3 equivalent.

[0147] In another preferred embodiment of the process according to the present invention, the wt % of said particles of quicklime having a particle size <90 μm and or said iron based compound is <40, preferably <38, more preferably <36% in order to influence the formation of monocalcium ferrites during thermal treatment.

[0148] In such a case, said thermal treatment is a thermal treatment at a temperature lower or equal to 1150° C., preferably lower or equal to 1100° C., more particularly higher or equal to 900° C., preferably according to the relationship (predetermined duration)/(thermal treatment temperature −1000° C.)>5, which allow to still further promote the formation of monocalcium ferrites.

[0149] In another preferred embodiment, the iron-based compound comprises at least 50 wt %, preferably at least 60 wt %, more preferably at least 70 wt %, more preferably at least 80 wt % and in a particular manner more than 95 wt % iron oxide under the form of hematite Fe_2O_3 relative to the total weight of the iron based compound expressed in Fe_2O_3 equivalent.

[0150] Other embodiments of the method according to the invention are presented in the accompanying claims.

[0151] The invention also relates to a composition in the form of green briquettes comprising at least one "quick" calcium-magnesium compound and an iron-based compound, characterized in that the composition comprises at least 40 wt % of CaO+MgO equivalent relative to the weight of said composition, said composition having a Ca/Mg molar ratio greater than or equal to 1, preferably greater than or equal to 2, more preferably greater than or equal to 3 and characterized in that said iron-based compound is present at a content of at least 20 wt %, preferably at least 25 wt %, in a preferred manner at least 30 wt %, more preferably at least 35 wt % of Fe_2O_3 equivalent relative to the weight of said composition, said iron-based compound having a very fine granulometric distribution characterized by a median size d_{50} below 100 μm, preferably below 50 μm and a size d_{90} below 200 μm, preferably below 150 μm, preferably below 130 μm, more preferably below 100 μm, wherein said at least one "quick" calcium-magnesium compound comprising at least 40 wt % of CaO+MgO equivalent comprises a fraction of particles of calcium-magnesium compound having a particle size ≤90 μm having at least 20 weight % CaO equivalent with respect to the weight of said pulverulent mixture, said composition having a Shatter test index lower or equal to 20% for iron oxide content lower than 40% and this, surprisingly even when the amount of fine particles is high.

[0152] This mechanical strength, evaluated by the Shatter test, for green briquettes having contents of iron-based compound below 40% is particularly interesting because these green briquettes may subsequently be thermally treated, according to one embodiment of the invention, in a rotary kiln in which these briquettes are therefore submitted to repeated drops.

[0153] In the sense of the present invention, said "quick" calcium-magnesium compound comprises one or more "quick" calcium-magnesium compounds.

[0154] The "quick" calcium-magnesium compound is selected from the group consisting of quicklime (calcium lime), magnesian lime, dolomitic quicklime, calcined dolomite and mixtures thereof, preferably in the form of particles, such as particles resulting from screening, from grinding, dusts from filters and mixtures thereof. Said "quick" calcium-magnesium compound may hence be regarded as a calcium-magnesium component of the composition under the form of briquettes, which latter may also comprise other compounds.

[0155] In a particular embodiment of the invention, said composition under the form of green briquettes according to the present invention comprises at most 97 wt %, preferably at most 90 wt %, preferably at most 88%, in certain embodiments at most 60 wt % of CaO+MgO equivalent relative to the weight of said composition.

[0156] In a preferred embodiment, the composition under the form of green briquettes according to the present invention comprises less than 10% of particles of "quick" calcium-magnesium compound having a particle size ≥90 μm and ≤5 mm relative to the total weight of the pulverulent mixture.

[0157] In another preferred embodiment, the composition under the form of green briquettes according to the present invention comprises between 10% and 60% of particles of "quick" calcium-magnesium compound having a particle size ≥90 μm and ≤5 mm relative to the total weight of the pulverulent mixture.

[0158] Advantageously, the wt % of CaO equivalent in the fraction of "quick" calcium-magnesium compound having a particle size <90 μm with respect to the total of the percentage in weight of quicklime in the fraction of calcium-magnesium compound having a particle size <90 μm and the % Fe_2O_3 equivalent of the iron-based compound having a very fine particle size distribution is ≥30%, preferably ≥32%, more preferably ≥34% and in a particularly preferred manner ≥36%.

[0159] Further, advantageously, the composition under the form of green briquettes according to the present invention comprises at least 50 wt %, preferably at least 60 wt %, more preferably at least 70 wt %, more preferably at least 80 wt % and in a particular manner more than 95 wt % iron oxide under the form of magnetite Fe_3O_4 relative to the total weight of the iron based compound expressed in Fe_2O_3 equivalent.

[0160] In another advantageous embodiment, the wt % of CaO equivalent in the fraction of "quick" calcium-magnesium compound having a particle size <90 μm with respect to the total of the percentage in weight of quicklime in the fraction of calcium-magnesium compound having a particle size <90 μm and the % Fe_2O_3 equivalent of the iron-based compound having a very fine particle size distribution is <40, preferably <38, more preferably <36%.

[0161] Further, advantageously, the composition under the form of green briquettes according to the present invention comprises at least 50 wt %, preferably at least 60 wt %, more preferably at least 70 wt %, more preferably at least 80 wt % and in a particular manner more than 95 wt % iron oxide under the form of hematite Fe_2O_3 relative to the total weight of the iron based compound expressed in Fe_2O_3 equivalent.

[0162] The present invention also relates to a composition in the form of thermally treated briquettes, comprising at least one iron-based compound, said composition comprising at least 40 wt % of CaO+MgO equivalent relative to the weight of said composition and having a Ca/Mg molar ratio greater than or equal to 1, preferably greater than or equal to 2, more preferably greater than or equal to 3, characterized in that said iron-based compound is present at a content of at least 20 wt %, preferably at least 25 wt %, in a preferred manner at least 30 wt %, more preferably at least 35 wt % of Fe_2O_3 equivalent relative to the weight of said composition, said iron-based compound comprising at least 60%, preferably at least 80%, and even more preferably at least 90% of calcium ferrite, expressed by weight of Fe_2O_3 equivalent, relative to the total weight of said iron-based compound expressed by weight of Fe_2O_3 equivalent, wherein at least 20 wt % calcium ferrite with respect to the weight of the composition under the form of thermally treated briquettes, wherein said calcium ferrite form a matrix wherein the particles of "quick" calcium-magnesium compound are dispersed.

[0163] Calcium ferrite is represented by the following formulae: $CaFe_2O_4$ (monocalcium ferrite) and/or $Ca_2Fe_2O_5$ (dicalcium ferrite).

[0164] Said matrix is to be understood as being a continuous phase based on calcium ferrite in which particles of "quick" calcium-magnesium compound, in particular quicklime, are dispersed. A distinction is made between the case when said particles of "quick" calcium-magnesium compound are of small size so that they melt visibly in the matrix based on calcium ferrite, and the case when particles of "quick" calcium-magnesium compound are of larger size and appear as inclusions of "quick" calcium-magnesium compound in said matrix.

[0165] The aforesaid distinction is made concrete on the basis of a section of a briquette according to the invention, applying scanning electron microscopy coupled to energy dispersive analysis. This provides visualization in two dimensions (the surface of the section) of an object initially in three dimensions (briquette), but also of the particles that make up the briquette. Thus, the particles of calcium-magnesium compound also appear in two dimensions on the section plane. As it is customary to liken particles in three dimensions to spheres and determine their size as the diameter of the equivalent sphere ("three-dimensional" size), in the present invention the cut surface of the particle is likened to an equivalent disk and its "two-dimensional" size to the equivalent diameter of this disk. More precisely, the two-dimensional sizes are calculated with a program that finds, for each particle of "quick" calcium-magnesium compound dispersed in the continuous matrix of calcium ferrite, the sum of the smallest and the largest dimension of its cut surface divided by two. This sum divided by two represents the diameter of the equivalent disk.

[0166] In this acceptation, it is considered that the particles of "quick" calcium-magnesium compound, melt or merge in said matrix (continuous phase) of calcium ferrite when said particles of "quick" calcium-magnesium compound have a two-dimensional size under 63 μm, observable by scanning electron microscopy coupled to energy dispersive analysis, in a section of the briquette.

[0167] In a particular embodiment of the invention, said pulverulent mixture comprises at most 97 wt %, preferably at most 90 wt %, preferably at most 88 wt %, in certain embodiments at most 60 wt % of CaO+MgO equivalent relative to the weight of said composition.

[0168] In a particular embodiment according to the present invention, when the composition is under the form of thermally treated briquettes, said "quick" calcium-magnesium compound comprises at least 10 wt %, preferably 20 wt %, more preferably 30 wt %, in a more preferable manner 40 wt % CaO+MgO equivalent, relative to the total weight of said composition.

[0169] Preferably, whether the composition is in the form of green or thermally treated briquettes, said "quick" calcium-magnesium compound contains fine particles rejected in screening in the production of pebbles of said calcium-magnesium compound, calcium-magnesium dust from filter at a concentration from 0 to 90 wt % relative to the total weight of said "calcium-magnesium" and from 10 to 100 wt

% of quicklime in the form of ground particles, relative to the total weight of said "quick" calcium-magnesium compound.

[0170] Preferably, whether the composition is in the form of green or thermally treated briquettes, said "quick" calcium-magnesium compound contains from 0 to 100 wt % quicklime in the form of ground particles from pebbles of said calcium-magnesium compound.

[0171] In a preferred variant according to the present invention, whether the composition is in the form of green or thermally treated briquettes, said "quick" calcium-magnesium compound contains from 0 to 90 wt % of fine particles rejected in screening in the production of pebbles of said calcium-magnesium compound and from 10 to 100 wt % of quicklime in the form of ground particles, relative to the total weight of said "quick" calcium-magnesium compound.

[0172] Advantageously, in the green or thermally treated briquettes, said quicklime in the form of ground particles is present at a concentration of at least 15 wt %, in particular at least 20 wt %, more preferably at least 30 wt %, especially preferably at least 40 wt % relative to the weight of the composition.

[0173] More particularly, whether the composition is in the form of green or thermally treated briquettes, said "quick" calcium-magnesium compound is a soft- or medium-burned calcium-magnesium compound, preferably soft-burned.

[0174] When quicklime in the form of ground particles is present, said quicklime in the form of ground particles is a soft-burned or medium-burned quicklime, preferably soft-burned.

[0175] More particularly, according to the present invention, when the composition is in the form of green briquettes, said composition has a BET specific surface area greater than or equal to 1 m^2/g, preferably greater than or equal to 1.2 m^2/g, more preferably greater than or equal to 1.4 m^2/g.

[0176] Advantageously, according to the present invention, when the composition is in the form of green briquettes, said composition has a porosity greater than or equal to 20%, preferably greater than or equal to 22%, more preferably greater than or equal to 24%.

[0177] The term "porosity of the composition in the form of briquettes" means, in the sense of the present invention, the total mercury pore volume determined by mercury intrusion porosimetry according to part 1 of standard ISO 15901-1:2005E, which consists of dividing the difference between the skeletal density, measured at 30000 psia, and the apparent density, measured at 0.51 psia, by the skeletal density.

[0178] Alternatively, porosity may also be measured by kerosene intrusion porosimetry. The density and the porosity of the briquettes are determined by kerosene intrusion, according to a measurement protocol derived from standard EN ISO 5017. The measurements are performed on 5 briquettes.

[0179] The density of the briquettes is calculated according to the formula $m1/(m3-m2)\times Dp$ and the percentage porosity according to the formula $(m3-m1)/(m3-m2)\times 100$.

[0180] m1 is the weight of these 5 briquettes, m2 is the weight of these 5 briquettes immersed in kerosene and m3 is the weight of these 5 "wet" briquettes, i.e. impregnated with kerosene. Dp is the density of the kerosene.

[0181] More particularly, according to the present invention, when the composition is in the form of green briquettes and the calcium-magnesium compound is mainly quicklime, said composition has a value of reactivity t_{60} below 10 min, preferably below 8 min, preferably below 6 min and even more preferably below 4 min. To take into account the content of iron-based compound in the composition, a little more than 150 g of said composition is added in the reactivity test, to have the equivalent of 150 g of quicklime added.

[0182] Advantageously, according to the present invention, when the composition is in the form of green briquettes and the calcium-magnesium compound is mainly burned dolomite, said composition has a value of reactivity t_{70} below 10 min, preferably below 8 min, preferably below 6 min and even more preferably below 4 min. To take into account the content of iron-based compound in the composition, a little more than 120 g of said composition is added in the reactivity test to have the equivalent of 120 g of burned dolomite added.

[0183] More particularly, according to the present invention, when the composition is in the form of thermally treated briquettes, said composition has a BET specific surface area greater than or equal to 0.4 m^2/g, preferably greater than or equal to 0.6 m^2/g, more preferably greater than or equal to 0.8 m^2/g.

[0184] Advantageously, according to the present invention, when the composition is in the form of thermally treated briquettes, said composition has a porosity greater than or equal to 20%, preferably greater than or equal to 22%, more preferably greater than or equal to 24%.

[0185] More particularly, according to the present invention, when the composition is in the form of thermally treated briquettes and the calcium-magnesium compound is mainly quicklime, said composition has a value of t_{60} below 10 min, preferably below 8 min, preferably below 6 min and even more preferably below 4 min. To take into account the content of iron-based compound in the composition, a little more than 150 g of said composition is added in the reactivity test to have the equivalent of 150 g of "free" quicklime added. "Free" quicklime means quicklime that has not reacted with iron oxide to give calcium ferrites $CaFe_2O_4$ and/or $Ca_2Fe_2O_5$.

[0186] In a preferred embodiment of the present invention, whether the composition is in the form of green or thermally treated briquettes, said at least one calcium-magnesium compound is formed from particles under 7 mm. Alternatively, said at least one calcium-magnesium compound is formed from particles under 5 mm. In another variant according to the present invention, said at least one calcium-magnesium compound is formed from particles under 3 mm.

[0187] In yet another variant of the present invention, whether the composition is in the form of green or thermally treated briquettes, said at least one calcium-magnesium compound is a mixture of particles under 7 mm and/or of particles under 5 mm and/or of particles under 3 mm.

[0188] In one embodiment of the invention, the composition in the form of green or thermally treated briquettes further comprises a binder or a lubricant, more particularly selected from the group consisting of binders of mineral origin such as cements, clays, silicates, binders of vegetable or animal origin, such as celluloses, starches, gums, alginates, pectin, glues, binders of synthetic origin, such as polymers, waxes, liquid lubricants such as mineral oils or silicones, solid lubricants such as talc, graphite, paraffins, stearates, in particular calcium stearate, magnesium stearate and mixtures thereof, preferably calcium stearate and/or magnesium stearate, at a content between 0.1 and 1 wt %, preferably between 0.15 and 0.6 wt %, more preferably between 0.2 and 0.5 wt % relative to the total weight of the composition.

[0189] The composition according to the present invention is a composition of green or thermally treated briquettes produced in industrial volumes and packaged in types of containers having a volume of contents greater than 1 m^3 such as big bags, containers, silos and the like, preferably sealed.

[0190] Advantageously, the briquettes of the composition in the form of green briquettes have a Shatter test index below 10%, for contents of iron oxide below 20 wt % of the composition.

[0191] Advantageously, the briquettes of the composition in the form of thermally treated briquettes have a Shatter test index below 8%, more particularly below 6%, regardless of the content of iron-based compound.

[0192] Advantageously, whether the composition is in the form of green or thermally treated briquettes, said briquettes have a largest dimension of at most 50 mm, preferably at most 40 mm, more preferably at most 30 mm. This means that the briquettes of the composition in the form of briquettes pass through a screen with square mesh with side of respectively 50 mm, preferably 40 mm, and in particular 30 mm.

[0193] Preferably, said green or thermally treated briquettes have a largest dimension of at least 10 mm, preferably at least 15 mm, more preferably at least 20 mm.

[0194] The term “a largest dimension” means a characteristic dimension of the green or thermally treated briquette that is largest, whether it is the diameter, length, width, thickness, preferably in the longitudinal direction of the briquette of oblong shape.

[0195] Preferably, whether the composition is in the form of green or thermally treated briquettes, said at least one calcium-magnesium compound is “quick” dolomite.

[0196] Alternatively, whether the composition is in the form of green or thermally treated briquettes, said at least one calcium-magnesium compound is quicklime.

[0197] Advantageously, said green or thermally treated briquettes have an average weight per briquette of at least 5 g, preferably at least 10 g, more preferably at least 12 g, and in particular at least 15 g.

[0198] According to the present invention, said green or thermally treated briquettes have an average weight per briquette less than or equal to 100 g, preferably less than or equal to 60 g, more preferably less than or equal to 40 g and in particular less than or equal to 30 g.

[0199] Advantageously, said green or thermally treated briquettes have an apparent density between 2 g/cm^3 and 3.0 g/cm^3, advantageously between 2.2 g/cm^3 and 2.8 g/cm^3.

[0200] In a preferred embodiment, the thermally treated briquettes according to the present invention comprise particles of “quick” calcium-magnesium compound, preferably particles of “quick” calcium-magnesium compound of two-dimensional size lower than 63 μm, observable by scanning electron microscopy coupled to energy dispersive analysis, in a section of said briquette and covering at least 20% of the area of said section.

[0201] In another preferred embodiment, the thermally treated briquettes according to the present invention further comprise particles of “quick” calcium-magnesium compound, preferably particles of “quick” calcium-magnesium compound of two-dimensional size above 63 μm and under 5 mm, observable by scanning electron microscopy coupled to energy dispersive analysis, in a section of said briquette and covering at most 20% of the area of said section and preferably at most 10% of the area of said section.

[0202] More particularly according to the present invention, the thermally treated briquettes further comprises particle of “quick” calcium-magnesium compound, preferably particles of “quick” calcium-magnesium compound of two-dimensional size above 63 μm and under 5 mm, observable by scanning electron microscopy coupled to energy dispersive analysis, in a section of said briquette and covering at least 20% of the area of said section and preferably at most 60% of the area of said section.

[0203] More particularly, the thermally treated briquettes according to the present invention comprise at least 40 wt %, preferably at least 50 wt % of the calcium ferrite are in the form of monocalcium ferrite $CaFe_2O_4$.

[0204] More particularly, the thermally treated briquettes according to the present invention comprise at least 40 wt %, preferably at least 50 wt % of the calcium ferrite are in the form of dicalcium ferrite $Ca_2Fe_2O_5$.

[0205] Other embodiments of the composition in the form of green or thermally treated briquettes according to the invention are presented in the accompanying claims.

[0206] The invention also relates to use of a composition in the form of green briquettes or in the form of thermally treated briquettes according to the present invention in iron and steel metallurgy, in particular in oxygen converters or in electric arc furnaces.

[0207] More particularly, the green or thermally treated briquettes according to the present invention are used in oxygen converters or in arc furnaces, mixed with briquettes of “quick” calcium-magnesium compounds or with pebbles of “quick” calcium-magnesium compounds.

[0208] In fact, during the first minutes of the refining process, there is insufficient slag available in the reaction vessel for effective commencement of the reaction of dephosphorization in the methods of the prior art. The use of the composition according to the present invention, i.e. doped with fluxes, which melts more quickly than limestone, helps to form a liquid slag earlier at the start of the process, in comparison with the conventional methods, owing to homogeneous mixing and shaping of this homogenized mixture, which makes it possible to accelerate the slag forming process even more and minimize the formation of slag components of high melting point, such as the calcium silicates that usually form in the aforementioned method of the prior art.

[0209] The invention also relates to the use of a composition in the form of green briquettes or in the form of thermally treated briquettes in a process for refining molten metal, in particular the dephosphorization of molten metal and/or desulphurization of molten metal and/or reduction of losses of refined metal in the slag.

[0210] The use of a composition in the form of green briquettes or in the form of thermally treated briquettes according to the present invention in a process for refining molten metal comprises

[0211] at least one step of introducing hot metal and optionally iron-based scrap in a vessel,

[0212] at least one step of introducing a composition in the form of green briquettes or in the form of thermally treated briquettes according to the present invention, preferably in the form of thermally treated briquettes according to the present invention,

[0213] at least one step of blowing oxygen into said vessel,

[0214] at least one step of forming a slag with said composition of briquettes in said vessel,

[0215] at least one step of obtaining refined metal having a reduced content of phosphorus compounds and/or sulphur compounds and/or an increased content of refined metal starting from hot metal by dephosphorization and/or desulphurization, and

[0216] at least one step of discharging said refined metal having a reduced content of phosphorus-containing and/or sulphur-containing components and/or an increased content of refined metal.

[0217] The use according to the present invention further comprises a step of adding quicklime, preferably quicklime in lumps or quicklime compacts, especially quicklime tablets or briquettes.

[0218] Other forms of use according to the invention are presented in the accompanying claims.

[0219] Other features, details and advantages of the invention will become clear from the description given hereunder, which is non-limiting and refers to the examples and to the figures.

[0220] FIG. **1** is a graph of the BET specific surface area and of kerosene intrusion porosity as a function of the content of Fe_2O_3 equivalent in the briquettes according to the present invention.

[0221] FIG. **2** is a graph of the Shatter test index (STI) as a function of the content of Fe_2O_3 equivalent in the thermally treated and green briquettes according to the present invention.

[0222] FIG. **3** is a graph of the percentage of $Fe_2 O_3$ converted to calcium ferrites as a function of the content of Fe_2O_3 equivalent in the thermally treated briquettes according to the present invention.

[0223] FIG. **4** is a graph of the variation of the content of calcium ferrites expressed as Fe_2O_3 equivalent in the thermally treated briquettes as a function of the iron oxide content expressed in Fe_2O_3 equivalent in the green briquettes before thermal treatment.

[0224] FIG. **5** shows photographs of sections of the briquettes according to examples 9 to 16.

[0225] The present invention relates to a method for briquetting fine particles of calcium-magnesium compounds and iron-based compound, said iron-based compound having a very fine granulometric distribution characterized by a median size d_{50} below 100 μm, preferably below 50 μm as well as a size d_{90} below 200 μm, preferably below 150 μm, preferably below 130 μm, more preferably below 100 μm.

[0226] The method of briquetting according to the invention comprises supplying an approximately homogeneous pulverulent mixture comprising at least 40 wt % of CaO+MgO equivalent of a "quick" calcium-magnesium compound and at least 20 wt %, preferably at least 25 wt %, in a preferred manner of at least 30 wt %, more preferably at least 35 wt % of an iron-based compound expressed in Fe_2O_3 equivalent relative to the weight of said composition, in which said quick calcium-magnesium compound comprising at least 40 wt % CaO+MgO equivalent further comprises at least a fraction of particles of calcium-magnesium compound having a particle size ≤90 μm, which latter further comprises at least 20 wt % CaO equivalent with respect to the weight of the pulverulent mixture.

[0227] In a particular embodiment of the invention, said pulverulent mixture comprises at most 97 wt %, preferably at most 90 wt %, preferably at most 88%, in certain embodiments at most 60 wt % of CaO+MgO equivalent relative to the weight of said composition.

[0228] The homogeneous mixture in which the iron-based compound is uniformly distributed is fed into a roller press, also sometimes called a tangential press, for example a Komarek, Sahut Konreur, Hosokawa Bepex, or Köppern press. In the roller press, the approximately homogeneous pulverulent mixture is compressed, optionally in the presence of a binder or a lubricant, more particularly selected from the group consisting of binders of mineral origin such as cements, clays, silicates, binders of vegetable or animal origin, such as celluloses, starches, gums, alginates, pectin, glues, binders of synthetic origin, such as polymers, waxes, liquid lubricants such as mineral oils or silicones, solid lubricants such as talc, graphite, paraffins, stearates, in particular calcium stearate, magnesium stearate, and mixtures thereof, preferably calcium stearate and/or magnesium stearate, at a content between 0.1 and 1 wt %, preferably between 0.15 and 0.6 wt %, more preferably between 0.2 and 0.5 wt % relative to the total weight of said briquettes.

[0229] In operation, the rollers of the roller press develop linear speeds at the periphery of the rollers between 10 and 100 cm/s, preferably between 20 and 80 cm/s, and linear pressures between 60 and 160 kN/cm, preferably between 80 and 140 kN/cm, and even more preferably between 80 and 120 kN/cm.

[0230] Assuming an angle of ½ degree at which the linear pressure is applied on the surface of the hoops, the surface pressure can be calculated, which is equal to the linear pressure divided by (½.π.D)/360, where D is the diameter of the hoops in cm. The surface pressure is between 300 and 500 MPa, preferably between 300 and 450 MPa, and more preferably between 350 and 450 MPa.

[0231] After compression, the calcium-magnesium composition is obtained in the form of green briquettes, which are collected.

[0232] In a preferred embodiment of the method according to the present invention, the green briquettes collected are treated thermally at a temperature between 900° C. and 1200° C., preferably between 1050° C. and 1200° C., more preferably between 1100° C. and 1200° C. inclusive. The thermal treatment is carried out preferably for a predetermined time of between 3 and 20 minutes, obtaining thermally treated briquettes in which said iron oxide is converted to calcium ferrite, i.e. thermally treated briquettes comprising a "quick" calcium-magnesium compound and a calcium ferrite compound present at a content of at least 3%, preferably at least 12%, more preferably at least 20%, preferably at least 30%, more preferably at least 35% of $Fe_2 O_3$ equivalent.

[0233] In one embodiment of the invention, said thermal treatment of the green briquettes is carried out in a rotary kiln at high temperature. Preferably, the rotary kiln is used for thermal treatment of briquettes whose iron oxide content is below 40%.

[0234] Alternatively, the thermal treatment is carried out in a horizontal kiln, for example a tunnel kiln, a through-type kiln, a car-type kiln, a roller kiln or a mesh band kiln. As a variant, any other type of conventional kiln may be used, provided it does not cause a change in the integrity of the compacts, for example through excessive attrition.

[0235] Cooling may either be performed conventionally in the downstream part of the kiln, or outside the kiln, for example in a vertical cooler in countercurrent for the cooling air or else in a fluidized-bed cooler with cooling air in the case of quenching.

[0236] In a particular embodiment, cooling at the end of the thermal treatment is carried out quickly, in less than 15 min, preferably in less than 10 min, in a fluidized bed with cooling air.

[0237] In a preferred embodiment according to the present invention, the method comprises, before said supplying of a homogeneous pulverulent mixture,

[0238] i. feeding a powder mixer with at least 40 wt % of CaO+MgO equivalent of a "quick" calcium-magnesium compound and with at least 20 wt %, preferably at least 25 wt %, more preferably at least 30 wt %, more preferably at least 35% of an iron-based compound expressed in Fe$_2$O3 equivalent having a very fine granulometric distribution characterized by a median size d_{50} below 100 μm, preferably below 50 μm as well as a size d_{90} below 200 μm, preferably below 150 μm, preferably below 130 μm, more preferably below 100 μm; said quick calcium-magnesium compound comprising at least 40 wt % CaO+MgO equivalent further comprises at least a fraction of particles of calcium-magnesium compound having a particle size ≤90 μm, which latter further comprises at least 20 wt % CaO equivalent with respect to the weight of the pulverulent mixture.

[0239] and

[0240] ii. mixing said "quick" calcium-magnesium compound with said iron-based compound for a predetermined length of time, sufficient to obtain an approximately homogeneous pulverulent mixture of said "quick" calcium-magnesium compound and of said iron-based compound.

[0241] In a variant of the invention, the calcium-magnesium compound comprises at least 10 wt % of ground quicklime particles, preferably at least 20 wt %, more particularly at least 30 wt % and at most 100 wt % relative to the total weight of said calcium-magnesium compound.

[0242] The "green" briquettes are based on quicklimes (optionally dolomitic) and ultrafine particles of iron oxide. They are characterized by an iron content by weight of at least 20 wt %, preferably at least 25 wt %, in a preferred manner of at least 30 wt %, more preferably at least 35 wt % expressed in Fe_2O_3 equivalent. The green briquettes are also characterized by a content by weight of calcium and magnesium of at least 40 wt %, expressed in CaO and MgO equivalent. Chemical analysis is performed by X-ray fluorescence spectrometry (XRF) according to standard EN 15309.

[0243] Semiquantitative chemical analysis by XRF for determining the relative concentration by weight of the elements whose atomic mass is between 16 (oxygen) and 228 (uranium) is carried out starting from the samples ground to 80 μm and formed into pellets. The sample is excited by a high-energy source (primary X-rays), and on recovering its original state of excitation, the sample emits secondary X-rays, characteristic of the chemical elements making up the sample.

[0244] The samples are put in a PANalytical/MagiX Pro PW2540 apparatus, operating in wavelength dispersion mode. Measurement is performed with a power of 50 kV and 80 mA, with a Duplex detector.

[0245] The analysis results give the calcium, magnesium and iron content and these measurements are reported in weight of CaO and MgO equivalent, and weight of Fe_2O_3 equivalent.

[0246] Semiquantitative analysis of the iron-based compounds (iron oxides Fe_2O_3, Fe_3O_4, calcium ferrites $CaFe_2O_4$, $Ca_2Fe_2O_5$) is carried out based on an X-ray diffraction pattern by the Rietveld method.

[0247] This method consists of simulating a diffraction pattern using a crystallographic model of the sample, then adjusting the parameters of this model so that the simulated diffraction pattern is as close as possible to the experimental diffraction pattern. At the end of semiquantitative analysis, it is verified that the total amount of iron expressed in Fe_2O_3 equivalent does not differ by more than 10% relative to the values obtained by XRF. The percentage of total iron in the form of calcium ferrites is obtained by simple division (Fe in the ferrites divided by Fe in all of the iron-based compounds).

[0248] The green briquettes are also characterized by a BET specific surface area greater than or equal to 1 m^2/g, preferably 1.2 m^2/g, preferably 1.4 m^2/g.

[0249] The porosity of the green briquettes is greater than or equal to 20%, preferably 22%, preferably 24%.

[0250] The green briquettes have an apparent density between 2.0 and 3.0 and preferably between 2.2 and 2.8.

[0251] The briquettes have good resistance to ageing. Thus, when they are exposed to a humid atmosphere containing for example 5 to 15 g/m^3 of absolute humidity, degradation of their mechanical properties (STI) only occurs beyond 1.5% of weight increase, preferably 2% of weight increase, and more preferably 2.5% of weight increase, following the reaction of hydration of quicklime CaO to slaked lime $Ca(OH)_2$.

[0252] The thermally treated briquettes comprise a calcium-magnesium compound, for example quicklimes (dolomitic) and an iron-based compound, containing ultrafine particles of iron oxide and calcium ferrites $CaFe_2O_4$ and/or $Ca_2Fe_2O_5$.

[0253] The thermally treated briquettes are characterized by an iron content by weight of at least 20 wt %, preferably at least 25 wt %, in a preferred manner of at least 30 wt %, more preferably at least 35 wt % expressed in Fe_2O_3 equivalent. They are also characterized by a content by weight of calcium and magnesium of at least 40 wt % expressed in CaO and MgO equivalent. Chemical analysis is carried out by XRF, as mentioned above.

[0254] At least 40%, preferably at least 50%, preferably at least 60% and more preferably at least 70% of the total iron is in the form of calcium ferrites.

[0255] Quantification of the calcium ferrites is performed by XRD/Rietveld analysis after grinding the briquettes, as for the green briquettes.

[0256] The thermally treated briquettes of the present invention have a Shatter test index ("STI", i.e. percentage by weight of fines below 10 mm after 4 drops from 2 m) below 6%, regardless of the content of iron-based compounds.

[0257] They are also characterized by a specific surface area greater than or equal to 0.4 m^2/g, preferably 0.5 m^2/g, preferably 0.6 m^2/g.

[0258] The porosity is greater than or equal to 20%, preferably 22%, preferably 24%.

[0259] The thermally treated briquettes have an apparent density between 2.0 and 3.0 and preferably between 2.2 and 2.8.

[0260] The thermally treated briquettes have good resistance to ageing. Thus, when they are exposed to a humid atmosphere containing for example 5 to 15 g/m^3 of absolute humidity, degradation of their mechanical properties (STI) only occurs beyond 4% of weight increase, preferably 4.5% of weight increase, and more preferably 5% of weight increase, following the reaction of hydration of quicklime CaO to slaked lime $Ca(OH)_2$.

EXAMPLES

Example 1

Preparation of Ground Quicklime Fines and Pilot Preparation of Briquettes

[0261] Quicklime fines from grinding were prepared from a soft-burned lump lime produced in a parallel-flow regenerative kiln. Grinding is performed in a hammer mill equipped with a 2-mm screen and a recycling loop for sizes above 2 mm. These quicklime fines from grinding contain 29% of particles having a particle size lower than 90 μm (d_{30}<90 μm), 71% of particles above 90 μm, 37% of particles above 500 μm, 21% of particles above 1 mm and 1% of particles between 2 and 3 mm. The value of t_{60} of the water reactivity test is 0.9 min. The BET specific surface area (measured by nitrogen adsorption manometry after vacuum degassing at 190° C. for at least two hours and calculated by the multipoint BET method as described in standard ISO 9277:2010E) is 1.7 m^2/g. These quicklime fines from grinding contain 95.7% of CaO and 0.8% of MgO by weight.

[0262] A Gericke GCM450 powder mixer is used, with a capacity of 10 dm^3, equipped with standard paddles with radius of 7 cm, rotating at 350 revolutions per minute (i.e. 2.6 m/s). This mixer is used in continuous mode for preparing a mixture consisting of:

[0263] quicklime fines from grinding,

[0264] iron oxide fines,

[0265] powdered calcium stearate.

[0266] The total flow rate of powder is 300 kg/h and the residence time is 3.5 s.

[0267] The mixture obtained is very homogeneous. This signifies that the Fe content for different 10 g samples taken from the final mixture is always plus or minus 5% of the mean value.

[0268] A tangential press is used, equipped with hoops with a diameter of 604 mm and width of 145 mm for producing briquettes with a theoretical volume of 7.2 cm^3 in the shape of a bar of soap (4 arrays of 67 pockets per hoop, or 268 pockets per hoop), capable of developing a linear pressure of up to 120 kN/cm.

[0269] Starting with 10 tonnes of the mixture, the tangential press is supplied and compaction is performed at a speed of 12 revolutions per minute (i.e. a linear speed of 38 cm/s) at a linear pressure of 120 kN/cm (or a calculated surface pressure of 455 MPa for an angle of 0.5 degree).

[0270] Several tonnes of briquettes are obtained having an average volume of 8.4 cm^3, an average weight of 21.4 g and an average density of 2.4. These briquettes have a length of about 36 mm, a width of about 26 mm and a thickness of about 15.8 mm. These briquettes develop a total mercury pore volume (determined by mercury intrusion porosimetry according to part 1 of standard ISO 15901-1:2005E, which consists of dividing the difference between the skeletal density, measured at 30000 psia, and the apparent density, measured at 0.51 psia, by the skeletal density).

[0271] The water reactivity of the briquettes is determined by adding a predetermined amount of these briquettes, previously ground to fines with a size between 0 and 1 mm, to 600 ml of water at 20° C. to correspond to 150 g of quicklime.

[0272] A Shatter test is carried out with 10 kg of these briquettes, performing 4 successive drops from 2 m. The amount of fines under 10 mm generated at the end of these 4 drops is weighed.

[0273] The granulometric distribution of the iron-based particles in the composition in briquette form is determined by scanning electron microscopy and X-ray mapping, coupled to image analysis.

[0274] The briquettes are also characterized by carrying out a thermal treatment (hot charge/discharge) on several of these briquettes, at the end of which a powder with granulometry under 80 μm is prepared. The latter is characterized by X-ray diffraction, and phase quantification is performed by Rietveld analysis.

Example 2 to 9

[0275] Green briquettes are prepared according to the invention with ground quicklime containing particles with sizes between 0 and 2 mm, but having different granulometric profiles and contents of iron oxide of the hematite type expressed in Fe_2O_3 equivalent ranging from 10% to 60 wt %. The iron oxide used in these examples is characterized by a d_{10} of 0.5 μm, d_{50} of 12.3 μm and d_{90} of 35.7 μm. In each example, the particles of ground quicklime with size between 0 and 2 mm have at least 30% of particles that are under 90 μm. The preparation protocol is described at example 1.

[0276] Green briquettes of identical composition were treated thermally at 1100° C. or at 1200° C. for 20 minutes to obtain thermally treated briquettes having different contents of quicklime and iron-based compounds. The composition of the briquettes and the thermal treatments carried out are presented in Table 2. Several tests were carried out on these green and thermally treated briquettes, and are described below with the aid of FIGS. **1** to **4**.

[0277] FIG. **1** is a graph showing:

[0278] the variation of the BET specific surface area as a function of the content of iron-based compound expressed in Fe_2O_3 equivalent, for green briquettes;

[0279] the variation of the porosity as a function of the content of iron-based compound expressed in Fe_2O_3 equivalent, for green briquettes;

[0280] the variation of the BET specific surface area as a function of the content of iron-based compound expressed in Fe_2O_3 equivalent, for thermally treated briquettes that have undergone thermal treatment of 1100° C. for 20 minutes; and

[0281] the variation of the porosity as a function of the content of iron-based compound expressed in Fe_2O_3 equivalent, for thermally treated briquettes that have undergone thermal treatment of 1100° C. for 20 minutes.

[0282] As can be seen, these variations of porosity and specific surface area show a slight linear decrease with the content of iron-based compound for the green and thermally treated briquettes. The thermally treated briquettes have a lower specific surface area than the green briquettes, whereas they have higher porosity for identical contents of iron-based compound.

[0283] FIG. **2** is a graph showing:

[0284] the variation of the Shatter test index for green briquettes, as a function of the contents of iron-based compound expressed in Fe_2O_3 equivalent; and

[0285] the variation of the Shatter test index for thermally treated briquettes that have undergone thermal treatment at a temperature of 1100° C. for 20 minutes, as a function of the contents of iron-based compound expressed in Fe_2O_3 equivalent.

[0286] As can be seen, the Shatter indices are below 20% for green briquettes having contents of iron-based compound expressed in Fe_2O_3 equivalent below 40%, whereas for the thermally treated briquettes, all the Shatter tests are below 10%, or even 6%.

[0287] FIG. **3** is a graph showing the variation of the yield of iron-based compound (iron oxide) converted to calcium ferrite, as a function of the iron oxide content expressed in Fe_2O_3 equivalent as well as the amount of iron oxide converted in monocalcium ferrite and dicalcium ferrite. The thermal treatment is done in static bed during 20 min at 1100° C. in a tunnel furnace on a 100 mm thickness of briquettes.

[0288] As can be seen, the yield in conversion to calcium ferrite begins to decrease for contents of iron oxide expressed in Fe_2O_3 equivalent above 40%. The percentage in monocalcium ferrites go through a maximum for amount of iron oxide of 40%. The percentage of the formation of dicalcium ferrites reduced with the iron oxide content.

[0289] FIG. **4** shows the variation of the content of calcium ferrites expressed in Fe_2O_3 equivalent in the thermally treated briquettes as a function of the iron oxide content expressed in Fe_2O_3 equivalent in the green briquettes before thermal treatment.

[0290] As can be seen, the contents of calcium ferrites in the thermally treated briquettes increase with the iron oxide content in the green briquettes. However, this variation passes through a maximum at 50% content of calcium ferrites for contents of iron oxide in the green briquettes in the range from 40 to 45%, and then decreases to contents of calcium ferrites of about 40% for contents of iron oxide in the green briquettes of 60%.

[0291] Nevertheless, it is possible to push the yield in conversion of iron oxide to calcium ferrites beyond 90% and obtain contents of calcium ferrites in the thermally treated briquettes beyond 50%, even beyond 70% for example by increasing the temperature of the thermal treatment to 1200° C. or by optimizing grinding of the quicklime so as to increase the profraction of quicklime particles smaller than 90 μm, or a combination of the two. Several examples were undertaken and the measurement results are presented in Table 1.

TABLE 1

Examples	% Fe_2O_3 equivalent	Thermal treatment temperature	Type of CaO	% conversion to calcium ferrites	% of calcium ferrites in the thermally treated briquette	% of $CaFe_2O_4$ in weight of calcium ferrite	% of $Ca_2Fe_2O_5$ in weight of calcium ferrite
Ex. 2	20%	1200° C.	CaO <2 mm, with 30% <90 μm	95%	31%	7	93
Ex. 3	30%	1200° C.	CaO <2 mm, with 30% <90 μm	98%	47%	22.5	77.5
Ex. 4	40%	1200° C.	CaO <2 mm, with 30% <90 μm	98%	58%	55.3	44.7
Ex. 5	50%	1200° C.	CaO <2 mm, with 30% <90 μm	97%	74%	39.4	60.6
Ex. 6	50%	1100° C.	50% of (CaO <2 mm, with 30% <90 μm) + 50% of CaO <90 μm	90%	65%	69.9	30.1
Ex. 7	50%	1100° C.	100% of CaO <90 μm	96%	73%	47.2	52.8
Ex. 8	50%	1200° C.	50% of (CaO <2 mm, with 30% <90 μm) + 50% of CaO <90 μm	99%	76%	43.9	56.1
Ex. 9	50%	1100° C.	CaO <2 mm, with 30% <90 μm	61%	43%		

[0292] As can be seen in Table 1, it is possible to optimize the various parameters of percentage of iron oxide, temperature of the thermal treatment, granulometry of the quicklime, so as to obtain yields in conversion of iron oxide to calcium ferrite above 70%, preferably above 80%, more preferably above 90% with at least 40 wt % of calcium ferrites in the form of monocalcium ferrites.

[0293] In example 4, thermally treated briquettes having a yield in conversion to calcium ferrite of 98% and containing 55.3 wt % of monocalcium ferrite relative to the amount of calcium ferrites are produced after thermal treatment at 1200° C. for 20 minutes on green briquettes containing about 40 wt % of hematite and 60 wt % of quicklime having a d_{97} equal to 2 mm and a d_{30} equal to 90μm, except for the presence of 0.25 wt % of calcium stearate, relative to the total weight of the green briquettes.

[0294] In example 6, thermally treated briquettes having a yield in conversion to calcium ferrite of 90% and containing 69.9 wt % of monocalcium ferrite relative to the amount of calcium ferrites are produced after thermal treatment at 1100° C. for 20 minutes on green briquettes containing about 50 wt % of hematite and 25 wt % of quicklime having a d_{97} equal to 2 mm and a d_{30} equal to 90 μm and 25 wt % of quicklime having a d_{97} equal to 90 μm, except for the presence of 0.25 wt % of calcium stearate, relative to the total weight of the green briquettes.

[0295] In example 7, thermally treated briquettes having a yield in conversion to calcium ferrite of 96% and containing 47.2 wt % of monocalcium ferrite relative to the amount of calcium ferrites are produced after thermal treatment at

1100° C. for 20 minutes on green briquettes containing about 50 wt % of hematite and 50 wt % of quicklime having a d_{97} equal to 90 μm.

[0296] In example 8, thermally treated briquettes having a yield in conversion to calcium ferrite of 99% and containing 43.9 wt % of monocalcium ferrite relative to the amount of calcium ferrites are produced after thermal treatment at 1200° C. for 20 minutes on green briquettes containing about 50 wt % of hematite and 25 wt % of quicklime having a d_{97} equal to 2 mm and a d_{30} equal to 90 μm, except for the presence of 0.25 wt % of calcium stearate, relative to the total weight of the green briquettes. The yield of monocalcium ferrite can be increased by reducing the thermal treatment temperature to 1100° C., except for the presence of 0.25 wt % of calcium stearate, relative to the total weight of the green briquettes.

[0297] In example 9, thermally treated briquettes having a yield in conversion to calcium ferrite of 61% and containing 82.6 wt % of monocalcium ferrite relative to the amount of calcium ferrites are produced after thermal treatment at 1100° C. for 20 minutes on green briquettes containing about 50 wt % of hematite and 50 wt % of quicklime having a d_{97} equal to 2 mm and a d_{30} equal to 90 μm. The yield of monocalcium ferrite can be increased by increasing the amount by weight of quicklime having a d_{100} equal to 90 μm, except for the presence of 0.25 wt % of calcium stearate, relative to the total weight of the green briquettes.

[0298] It may be advantageous in a metal refining process to have an amount of monocalcium ferrite above 40 wt %, as monocalcium ferrite has a lower melting point than dicalcium ferrite, and this may accelerate dissolution of the briquettes in the slag.

[0299] It is also possible to optimize the various parameters of percentage of iron oxide, temperature of the thermal treatment, granulometry of the quicklime, so as to obtain yields in conversion of iron oxide to calcium ferrite above 70%, preferably above 80%, more preferably above 90% with at least 40 wt % of calcium ferrites in the form of dicalcium ferrites. Although, as in example 7, it is possible to obtain, at 1100° C. for 20 minutes, 52.8% of dicalcium ferrites relative to the amount of calcium ferrites, most of the other examples show that the formation of at least 40% of dicalcium ferrites relative to the amount of calcium ferrites is promoted when the briquettes are submitted to a thermal treatment of 1200° C. for 20 minutes.

[0300] It may be advantageous to optimize the parameters of the method in order to obtain at least 40% dicalcium ferrites relative to the weight amount of calcium ferrites, to obtain a higher dicalcium ferrites and a melting temperature higher than the meting temperature of monocalcium ferrites and hence to minimize the risk of melting of the briquettes in the furnace.

[0301] FIG. **5** shows photographs of the sections of the briquettes from examples 9 to 16. The textures of the thermally treated briquettes from examples 9 to 16 were analysed by scanning electron microscopy coupled to energy dispersive analysis, by preparing a section of these briquettes, by encapsulating these briquettes in a resin, and by polishing the surface of the section. These analyses make it possible to construct a map of the distribution of each element in a section of the briquettes. Using image analysis software, it is possible to combine the maps obtained for each element and measure the size distribution and the relative coverage of each element.

[0302] It has thus been shown for the briquettes from examples 2 to 9 that calcium ferrite forms a matrix (or continuous phase) in which particles of quicklime (discontinuous phase) are dispersed. A calcium ferrite matrix can be obtained after thermal treatment for 20 minutes at temperatures between 900° C. and 1200° C., preferably between 1050 and 1200° C., of green briquettes containing at least 20 wt % of particles of calcium-magnesium compound, preferably in the form of quicklime and at least 20 wt % of iron oxide having a d_{90} under 200 μm, preferably under 150 μm, more preferably under 100 μm and a d_{50} below 50. The two-dimensional sizes of the particles of lime dispersed in the matrix are calculated by a program that finds the average of the smallest and largest dimension of each particle of quicklime in the calcium ferrite matrix. The particles are classified in a first group of particles whose two-dimensional size is under 63 μm and above the limit of detection of the measuring equipment, and a second group of particles whose two-dimensional size is above 63 μm. Table 2 below shows, for the briquettes from examples 2 to 9, the relative coverage of the calcium ferrite matrix, of the particles of quicklime under 63 μm and of the particles of quicklime above 63 μm in the cut section from each briquette.

TABLE 2

	Ex 2	Ex 3	Ex 4	Ex 5	Ex 6	Ex 7	Ex 8	Ex 9
Matrix (% surface coverage)	41	50	52	72	70	83	80	54
CaO <63 μm (% surface coverage)	2	3	2	4	8	11	4	4
CaO >63 μm (% surface coverage)	56	47	46	24	22	6	17	42

[0303] The percentages of surface coverage of the particles of quicklime above 63 μm are less than 25% for thermally treated briquettes having contents of calcium ferrites above 60 wt % of the composition.

Example 10

[0304] green briquettes were prepared with 38.85 wt % of iron oxide in the form of magnetite Fe_2O_4 having a d_{97} of 150 μm and a d_{50} of 40 μm with 60.9 wt % of quicklime having a d97 below 2 mm and a d_{30} below 90 μm as well as 0.25 wt % of calcium stearate, relative to the weight of the briquette. Thermal treatment was carried out on a static bed of three layers of briquettes for 20 min at 1100° C. in order to obtain thermally treated briquettes and the percentage by weight of iron converted to monocalcium ferrite is 8% whereas the percentage of iron converted to dicalcium ferrite is 82%.

Example 11

[0305] green briquettes were prepared with 39.9 wt % of iron oxide in the form of hematite Fe_2O_3 characterized by a d_{10} of 0.5 μm, d_{90} of 12.3 μm and d_{90} of 35.7 μm and with 59.85 wt % of quicklime having a d_{97} below 2 mm and a d_{30} below 90 μm and 0.25 wt % of calcium stearate relative to the weight of the briquette. The green briquettes obtained were treated thermally in the same conditions as in example 17 in order to obtain thermally treated briquettes. In this case, the percentage of iron converted to monocalcium ferrite is 65 wt % and the percentage of iron converted to dicalcium ferrite is 24 wt %.

Examples 12 to 28

Pre-Treatment under Modified Atmosphere Containing CO_2 Corresponding Respectively to Tests 1 to 17 in Table 3

[0306] In the following examples, compressive strength tests were performed on the briquettes using a Pharmatron Multitest 50, one of the plates of which is equipped with a point. The presence of a point reduces the force necessary to cause rupture of the briquettes relative to a compressive strength test carried out without the point.

[0307] 10 green briquettes containing 59.85 wt % of quicklime similar to that used in example 1, 39.9% of Fe_2O_3 from example 11 and 0.25% of calcium stearate were characterized by this compressive strength test. The average value is 33 kg-force.

[0308] Several pre-treatment tests were carried out, varying the parameters as indicated in Table 4, each time charging 10 new green briquettes in an 11-litre electric muffle furnace. All these pre-treatments were carried out between 20 and 450° C. under a flow of 10 litres per minute of a gas mixture formed from N_2, H_2O and CO_2. The ramps of temperature rise are between 2 and 10° C./min.

[0309] The concentrations by volume of H_2O in the gas are between 3.9 and 20.1%. The concentrations by volume of CO_2 in the gas are between 0.9 and 9.1%.

[0310] At the end of the pre-treatment, for each test, the 10 briquettes were characterized by compressive strength testing. In addition, all 10 pre-treated briquettes were analysed to determine the weight gains relating to hydration $dm(H_2O)/m$ and to carbonation $dm\ (CO_2)/m$. All of the results are presented in Table 3.

[0311] As can be seen, beyond 2 vol % of CO_2 in the gas forming the modified atmosphere, the pre-treatment leads to consolidation of the briquettes. Conversely, below 2 vol % of CO_2, the briquettes become less cohesive.

TABLE 3

	Thermal pre-treatment			Characterization of the thermally pre-treated briquettes			
	T (° C./min)	H2O (% vol)	CO2 (% vol)	dm (CO2/m %)	dm (H2O)/m (%)	crush test (Kg-force)	variation in the crush test (%)
Essai1	3.0	6.0	2.0	0.74	0.73	55	67%
Essai 2	9.0	6.0	2.0	0.43	0.44	50	52%
Essai 3	3.0	18.0	2.0	0.95	1.57	43	29%
Essai 4	9.0	18.0	2.0	0.42	1.03	33	−1%
Essai 5	3.0	6.0	8.0	2.23	0.20	60	82%
Essai 6	9.0	6.0	8.0	1.26	0.24	49	48%
Essai 7	3.0	18.0	8.0	2.51	0.90	51	55%
Essai 8	9.0	18.0	8.0	1.03	0.87	44	33%
Essai 9	1.9	12.0	5.0	3.29	0.59	60	83%
Essai 10	10.1	12.0	5.0	0.77	0.69	46	40%
Essai 11	6.0	3.9	5.0	1.08	0.24	49	47%
Essai 12	6.0	20.1	5.0	1.21	1.07	49	49%
Essai 13	6.0	12.0	0.9	0.13	1.32	9	−74%
Essai 14	6.0	12.0	9.1	1.82	0.46	60	81%
Essai 15	6.0	12.0	5.0	1.03	0.64	45	35%
Essai 16	6.0	12.0	5.0	1.11	0.51	49	48%
Essai 17	6.0	12.0	5.0	1.25	0.68	57	74%

Legend:
Essai = test

Comparative Example 4

[0312] The Shatter indices were compared with the compressive force for several samples of green briquettes to establish the correlation between the Shatter index and the compressive force. The green briquettes tested comprised quicklime with particle size between 0 and 3 mm with different contents of iron oxide, from 0 to 60 wt % and different contents of lubricant, ranging from 0.125 to 0.5 wt %, relative to the total weight of the briquettes. The parameters of the briquetting process were also altered to ensure that the population was large enough for establishing the correlation.

[0313] A compressive force of greater than 144 kg, corresponding to 317.5 pounds, is required for briquettes having a Shatter index below 10%.

[0314] Of course, the present invention is not in any way limited to the embodiments described above, and a great many modifications may be made to it while remaining within the scope of the appended claims.

1. Method for manufacturing a calcium-magnesium composition in the form of briquettes, comprising the following steps:

i. supplying a pulverulent mixture comprising at least one “quick” calcium-magnesium compound, said mixture comprising at least 40 wt % of CaO+MgO equivalent relative to the weight of said composition and having a Ca/Mg molar ratio greater than or equal to 1, preferably greater than or equal to 2, more particularly greater than or equal to 3 and an iron-based compound having a very fine granulometric distribution characterized by a median size d_{50} below 100 μm, preferably below 50 μm as well as a size d_{90} below 200 μm, preferably below 150 mμm, preferably below 130 μm, more preferably below 100 μm;

feeding a roller press with said mixture,

iii. compressing said pulverulent mixture in said roller press, the rollers of the roller press developing linear speeds at the periphery of the rollers between 10 and 100 cm/s, preferably between 20 and 80 cm/s, and linear pressures between 60 and 160 kN/cm, preferably between 80 and 140 kN/cm, and even more preferably between 80 and 120 kN/cm, obtaining a calcium-magnesium composition in the form of green briquettes, and

iv. collecting said green briquettes,

wherein said at least one “quick” calcium-magnesium compound comprising at least 40 wt % CaO+MgO equivalent further comprises at least a fraction of particles of calcium-magnesium compound having a particle size ≤90 μm having at least 20 weight % CaO equivalent with respect to the weight of said pulverulent mixture, and wherein said iron-based compound being present at a content of at least 20 wt %, preferably at least 25 wt %, more preferably at least 30 wt %, in particular at least 35 wt % relative to the weight of said composition.

2. Method according to claim **1**, in which said compression step is effected in the presence of a binder or a lubricant, more particularly selected from the group consisting, of binders of mineral origin such as cements, clays, silicates, binders of vegetable or animal origin, such as cell loses, starches, gums, alginates, pectin, glues, hinders of synthetic origin, such as polymers, waxes, liquid lubricants such as mineral oils or silicones, solid lubricants such as talc, graphite, paraffins, stearates, in particular calcium stearate, magnesium stearate and mixtures thereof, preferably calcium stearate and/or magnesium stearate, at a content between 0.1 and 1 wt %, preferably between 0.15 and 0.6 wt %, more preferably between 0.2 and 0.5 wt % relative to the total weight of said briquettes.

3. Method according to claim **1**, further comprising a thermal treatment of said green briquettes at a temperature comprised between 900° C. and 1200° C. preferably between 1050° C. and 1200° C. included, preferably comprised between 1100° C. and 1200° C. included.

4. Method according to claim **1**, wherein said thermal treatment of green briquettes occur for a predetermined duration of between 3 and 20 minutes preferably greater than or equal to 5 minutes and less than or equal to 15 minutes.

5. Method according to claim **1**, in which said "quick" calcium-magnesium compound is quicklime.

6. Method according to claim **1**, further comprising, before said supplying of a homogeneous pulverulent mixture,

v. feeding a mixer with at least 40 wt % of CaO+MgO equivalent of a "quick" calcium-magnesium compound relative to the weight of said composition and with at least 20 wt %, preferably at least 25 wt %, more preferably at least 30 wt %, more preferably at least 35 wt % of Fe_2O_3 equivalent of an iron-based compound relative to the weight of said composition, said iron-based compound having a very fine granulometric distribution characterized by a median size d_{50} below 100 μm, preferably below 50 μm as well as a size d_{90} below 200 μm, preferably below 150 μm, preferably below 130 μm, more preferably below 100 μm; said at least one "quick" calcium-magnesium compound comprising at least 40 wt % of CaO+MgO equivalent comprises a fraction of particles of calcium-magnesium compound having a particle size ≤90 μm having at least 20 weight % CaO equivalent with respect to the weight of said pulverulent mixture,

vi. mixing said "quick" calcium-magnesium compound with said iron-based compound for a predetermined length of time, sufficient to obtain an approximately homogeneous pulverulent mixture of said "quick" calcium-magnesium compound and of said iron-based compound.

7. Method according to claim **6**, in which said binder or lubricant is added to the mixer, and in which said binder or lubricant is included in said pulverulent mixture, preferably homogeneous.

8. Method according to claim **1**, in which said "quick" calcium-magnesium compound contains at least 10 wt % of quicklime in the form of ground particles.

9. Method according to claim **1**, further comprising a pre-treatment step of the briquettes under modified atmosphere containing at least 2 vol % CO_2 and at most 30 vol % CO_2, preferably at most 20 vol % CO_2, more preferably at most 15 vol % CO_2, even more preferably at most 10 vol % CO_2 with respect to the modified atmosphere.

10. Method according to claim **1**, wherein said pulverulent mixture further comprises at least 10% of particles of "quick" calcium-magnesium compound having a particle size ≥90 μm and ≤5 mm with respect to the weight of the pulverulent mixture.

11. Method according to claim **1**, wherein said pulverulent mixture further comprises between 10% and 60% of particles of "quick" calcium-magnesium compound having a particle size ≥90 μm and ≤5 mm with respect to the weight of the pulverulent mixture.

12. Method according to claim **1**, wherein the weight percentage of CaO equivalent in the fraction of "quick" calcium-magnesium compound having a particle size <90 μm relative to the total of the weight percentage of quicklime in the fraction of calcium-magnesium compound having a particle size <90 μm and the % of Fe_2O_3 equivalent of said iron-based compound having a very fine granulometric distribution is ≥30%, preferably ≥32%, more preferably ≥34%, in a particularly preferred manner ≥36%.

13. Method according to claim **12**, wherein said thermal treatment is a thermal treatment at a temperature higher than or equal to 1100° C. preferably higher than or equal to 1150° C., preferably lower than or equal to 1200° C., preferably according to the rule (predetermined duration)/(thermal treatment temperature−1000° C.)>5.

14. Method according to claim **12**, wherein said iron-based compound comprises at least 50 weight %, preferably at least 60 weight %, more preferably at least 70 weight %, more preferably at least 80 weight % and particularly more than 95 weight % of iron oxide under the form of magnetite Fe_3O_4 expressed in Fe_2O_3 equivalent with respect to the total weight of the iron-based compound.

15. Method according claim **1**, wherein the weight percentage of CaO equivalent in the fraction of "quick" calcium-magnesium compound having a particle size <90 μm relative to the total of the weight percentage of quicklime in the fraction of calcium-magnesium compound having a particle size <90 μm and the % of Fe_2O_3 equivalent of said iron-based compound having a very fine granulometric distribution is <40, preferably <38, more preferably <36% and higher than 20%, preferably higher than 22%, preferably 24%.

16. Method according to claim **15**, wherein said thermal treatment is a thermal treatment at a temperature lower than or equal to 1150° C. preferably lower than or equal to 1100° C., preferably higher than or equal to 900° C., preferably according to the rule (predetermined duration)/(thermal treatment temperature−1000° C.)>5.

17. Method according to claim **15**, wherein said iron-based compound comprises at least 50 weight %, preferably at least 60 weight %, more preferably at least 70 weight %, more preferably at least 80 weight % and particularly more than 95 weight % of iron oxide under the form of hematite Fe_2O_3 expressed in Fe_2O_3 equivalent with respect to the total weight of the iron-based compound.

18. Composition in the form of green briquettes comprising at least one "quick" calcium-magnesium compound and art iron-based compound, characterized in that the composition comprises at least 40 wt % of CaO+MgO equivalent relative to the weight of said composition, said composition having a Ca/Mg molar ratio greater than or equal to 1, preferably greater than or equal to 2, more preferably greater than or equal to 3 and characterized in that said iron-based compound is present at a content of at least 20 wt %, preferably at least 25 wt %, more preferably at least 30 wt %, In a preferred manner at least 35 wt % of Fe_2O_3 equivalent relative to the weight of said composition, said iron-based compound having a very fine granulometric distribution characterized by a median size d_{50} below 100 μm, preferably below 50 μm as well as a size d_{90} below 200 μm, preferably below 150 μm, preferably below 130 μm, more preferably below 100 μm, wherein said at least one "quick" calcium-magnesium compound comprising at least 40 wt % of CaO+MgO equivalent comprises a fraction of particles of calcium-magnesium compound having a particle size ≤90 μm having at least 20 weight % CaO equivalent with respect to the weight of said pulverulent mixture.

19. Composition in the form of green briquettes according to claim **18**, in which said calcium-magnesium compound is quicklime.

20. Composition in the form of green briquettes according to claim **18**, in which said "quick" calcium -magnesium compound comprises:

- fine particles of calcium-magnesium compound selected from fine particles rejected in screening in the production of the pebbles of said "quick" calcium-magnesium compound, calcium-magnesium filter dust at a concentration from 0 wt % to 90 wt % relative to the total weight of said "quick" calcium-magnesium compound, and
- from 10 to 100 wt % of quicklime in the form of ground particles, relative to the total weight of said "quick" calcium-magnesium compound.

21. Composition in the form of green briquettes according to claim **18**, having a BET specific surface area greater than or equal to 1 m^2/g, preferably greater than or equal to 1.2 m^2g, more preferably greater than or equal to 1.4 m^2/g.

22. Composition in the form of green briquettes according to claim **18**, having a porosity greater than or equal to 20%, preferably greater than or equal to 22%, more preferably greater than or equal to 24%.

23. Composition in the form of green briquettes according to claim **18**, further comprising a binder or a lubricant, more particularly selected from the group consisting of binders of mineral origin such as cements, clays, silicates, binders of vegetable or animal origin, such as celluloses, starches, gums, alginates, pectin, glues, binders of synthetic origin, such as polymers, waxes, liquid lubricants such as mineral oils or silicones, solid lubricants such as talc, graphite, paraffins, stearates, in particular calcium stearate, magnesium stearate, and mixtures thereof, preferably calcium stearate and/or magnesium stearate, at a content between 0.1 and 1 wt %, preferably between 0.15 and 0.6 wt %, more preferably between 0.2 and 0.5 wt % relative to the total weight of said briquettes.

24. Composition in the form of green briquettes according to claim **18**, further comprising at least 10% of particles of "quick" calcium-magnesium compound having a particle size ≥90 μm and ≤5 mm relative to the total weight of the pulverulent mixture.

25. Composition in the form of green briquettes according to claim **18**, further comprising between 10% and 60% of particles of "quick" calcium-magnesium compound having a particle ≥90 μm and ≤5 mm relative to the total weight of the pulverulent mixture.

26. Composition in the form of green briquettes according to claim **18**, wherein the weight percentage of CaO equivalent in the fraction of "quick" calcium-magnesium compound having a particle size <90 μm relative to the total of the weight percentage of quicklime in the fraction of calcium-magnesium compound having a particle size <90 μm and the of Fe_2O_3 equivalent of said iron-based compound having a very fine granulometric distribution is ≥30%, preferably ≥32%, more preferably ≥34% and particularly preferably ≥36%.

27. Composition in the form of green briquettes according to claim **18**, comprising further at least 50 weight %, preferably at least 60 weight %, more preferably at least 70 weight %, more preferably at least 80 weight % and particularly more than 95 weight % of iron oxide under the form of magnetite Fe_3O_4 expressed in Fe_2O_3 equivalent with respect to the total weight of the iron-based compound.

28. Composition in the form of green briquettes according to claim **18**, wherein the weight percentage of CaO equivalent in the fraction of "quick" calcium-magnesium compound having a particle size <90 μm relative to the total of the weight percentage of quicklime in the fraction of calcium-magnesium compound having a particle size <90 μm and the % of Fe_2O_3 equivalent of said iron-based compound having a very fine granulometric distribution is <40, preferably <38, more preferably <36% and higher than 20%, preferably higher than 22%, preferably 24%,

29. Composition in the form of green briquettes according to claim **18**, further comprising at least 50 weight %, preferably at least 60 weight, more preferably at least 70 weight %, more preferably at least 80 weight % and particularly more than 95 weight % of iron oxide under the form of hematite Fe_2O_3 expressed in Fe_2O_3 equivalent with respect to the total weight of the iron-based compound.

30. Composition in the form of thermally treated briquettes, comprising at least one iron-based compound, said composition comprising at least 40 wt % of CaO+MgO equivalent relative to the weight of said composition and having a Ca/Mg molar ratio greater than or equal to 1, preferably greater than or equal to 2, more preferably greater than or equal to 3, characterized in that said iron-based compound is present at a content of at least 20 wt %, preferably at least 25 wt %, in a preferred manner at least 30 wt %, more preferably at least 35 wt % of Fe_2O_3 equivalent relative to the weight of said composition, said iron-based compound comprising at least 60% of calcium ferrite, expressed by weight of Fe_2O_3 equivalent, relative to the total weight of said iron-based compound expressed by weight of Fe_2O_3 equivalent and wherein at least 20 wt % calcium ferrites with respect to the weight of the composition in the form of thermally treated briquettes, wherein said calcium ferrite forms a matrix wherein "quick" calcium-magnesium compound are dispersed.

31. Composition in the form of thermally treated briquettes according, to claim **30**, in which said iron-based compound comprises at least 70%, preferably at least 80%, and even more preferably at least 90 wt % of calcium ferrite relative to the total weight of said iron-based compound.

32. Composition in the form of thermally treated briquettes according to claim **30**, having a BET specific surface area greater than or equal to 0.4 m^2/g, preferably greater than or equal to 0.6 m^2/g, more preferably greater than or equal to 0.8 m^2 g.

33. Composition in the form of thermally treated briquettes according to claim **30**, having a porosity greater than or equal to 20%, preferably greater than or equal to 22%, more preferably greater than or equal to 24%.

34. Composition in the form of thermally treated briquettes according to claim **30**, in which the thermally treated briquettes have a Shatter test index below 8%, preferably below 6%, preferably below 4%, and more preferably below 3%, in particular below 2%.

35. Composition in the form of thermally treated briquettes according to claim **30**, characterized in that it further comprises particles of "quick" calcium-magnesium compound, preferably particles of quicklime having a two-dimensional size above 63 μm and under 5 mm, observable by scanning electron microscopy coupled to energy dispersive analysis, in a section of said briquette and covering at most 20% of the area of said section and preferably at most 10% of the area of said section.

36. Composition in the form of thermally treated briquettes according to claim **30**, characterized in that it further comprises particles of "quick" calcium-magnesium compound, preferably particles of quicklime having a two-dimensional size above 63 μm and under 5 mm, observable by scanning electron microscopy coupled to energy dispersive analysis, in a section of said briquette and covering at least 20% of the area of said section and preferably at most 60% of the area of said section.

37. Composition in the form of thermally treated briquettes, comprising at least one iron-based compound according to claim **30**, wherein at least 40 wt %, preferably 50 wt % of calcium ferrites are in the form of monocalcium ferrite $CaFe_2O_4$.

38. Composition in the form of thermally treated briquettes, comprising at least one iron-based compound according to claim **30**, wherein at least 40 wt %, preferably 50 wt % of calcium ferrites are in the form of dicalcium ferrite $Ca_2Fe_2O_5$.

39-43. (canceled)

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