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(54) **PROCESS FOR PREPARING OPTIMIZED CALCINED, IRON- AND CHROME-CONTAINING PELLETS**

(57) The invention provides a process for preparing calcined, iron- and chrome-containing pellets comprising the steps
a) producing pellets comprising mixing chrome ore material, Chrome Ore Process Residue (COPR) and a saccharide binder,
b) optionally drying the pellets obtained by step a), and
c) calcining the pellets,
as well as novel calcined, iron- and chrome-containing pellets obtainable by said process.

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Description

[0001] The invention relates to a process for preparing calcined, iron- and chrome-containing pellets, to calcined, iron- and chrome-containing pellets and their use for the preparation of Ferrochrome as well as to a process for the preparation of Ferrochrome using the calcined, iron- and chrome-containing pellets.

[0002] A widely used iron- and chrome-containing alloy is the so called Ferrochrome. Ferrochrome is used in the stainless-steel industry to increase the resistivity of steel against water and air to prevent the formation of rust. The iron and chrome source for the Ferrochrome production is usually chromite, a chrome ore, which is found in some parts of the world, like in South Africa.

[0003] The production of Ferrochrome is usually carried out in huge electrically heated arc furnaces or blast furnaces at high temperatures, using a carbon based reductant which can be part of the electrode or which is mixed in the chrome ore, or both. The consumption of electricity is significant and determines the cost effectiveness of a process using electrically heated furnaces. The process results in a liquid, molten alloy which is casted in casts, and a layer of partially molten residue floating on top of the liquid metal, the slag.

[0004] The usage of fine chrome ore material, so called "fines" or "flour", is economically of interest, because it decreases the necessary dwell time of the ore in the melt during reduction process significantly, but is practically difficult. In the arc furnaces a strong stream of hot gas is formed which results in an upstream. The particles of the fines are too small to be dropped into the furnace: they would not reach the hottest zones (melt) for reduction. Most of this material would be blown out of the furnace with the off-gas stream. In order to get the fines in a suitable shape pellets were formed out of the fines as disclosed in ZA2004-03429A. In Minerals Engineering (2012), 34, 55-62, a detailed description of the used binders and their properties and effects on the pellet strength and other properties are given.

[0005] The pellets produced according to the process of ZA2004-03429A and according to Minerals Engineering (2012), 34, 55-62, are made of chrome ore, a carbonaceous reductant and a so-called unconverted or non-activated binding agent. The binding agent is a mainly silica based clay, like Bentonite. Bentonite comprises ca. 24 wt% of silicon.

[0006] Besides inorganic binders organic binders (organic binder additives) were tested and disclosed, e.g. Carboxymethylcellulose. The usage is limited to strength improvement in low temperature regimes as "wet green pellets" at room temperature as discussed in O. Sivrikaya, A. I. Arol (2013) Method to improve preheated and fired strengths of haematite pellets using boron compounds with organic binders, Ironmaking & Steelmaking, 40:1, 1-8, DOI: 10.1179/1743281212Y.0000000016.

[0007] There are some disadvantages of using inorganic, clay-based binders and the pellets produced according to this process: the binding agent Bentonite contains neither iron nor chrome and thus, cannot contribute to the formation of Ferrochrome afterwards. Instead, the silica contained in Bentonite increases the amount of useless and costly slag. Slag is not only an undesired by-product in the process for the production of Ferrochrome but furthermore its formation requires additional electrical energy (e.g. for heating and for the reduced throughput of the furnace). Another disadvantage of the process is the effect of Bentonite on the density of the wet pellets fed into a tunnel furnace for pre-calcining step. The Bentonite is absorbing water and decreases the density of the pellets, which leads to a lower throughput of material through the tunnel furnace, as this is limited by volume per time unit, but the producer get paid by mass of pellets produced. On the other hand, the pore volume of the pellets is important, as the reducing gases formed in the arc furnace process need to reach the oxides in the pellets. So, a higher Chrome content and an increased density of the raw, dried pellets is desired with only small changes in the porosity of the indurated, calcined pellets. This results in lower slag production, higher throughput through the (tunnel-) furnace.

[0008] WO2018172284A1 discloses a method for producing pre-reduced calcined, iron- and chrome-containing pellets, wherein chromite ore material and COPR are mixed with large amounts of a reductant component and subsequently reduced at temperatures of 1250°C to 1600°C in an inert or reducing atmosphere. However, while the process according to said process yields calcined pellets with a higher cold crush strength compared to pellets obtained by using bentonite binder, they have a lower density than the latter.

[0009] Furthermore, the yet unpublished patent application EP18196811.6 describes the usage of COPR as binder in the absence of reductant. However, said use results in calcined pellets with a higher density compared to pellets obtained by using bentonite binder, but at the same time, they suffer of a lower cold crush strength compared to the latter.

[0010] Organic binders are expected to have no large impact on the cold crush strength after firing, as they burn off at low temperatures below 500°C.

[0011] Hence, it was the object of the present invention to avoid the disadvantages of the prior art to provide a process for preparing calcined, iron- and chrome-containing pellets suitable for use for the preparation of ferrochrome that combines a reduced slag formation and leads to calcined pellets having a high cold crush as well as a high density.

[0012] It was surprisingly found, that this object can be achieved by the process according to the claims of the present patent application.

[0013] The invention therefore provides a process for preparing calcined, iron- and chrome-containing pellets comprising the steps:

a) mixing chrome ore material, COPR and saccharide binder and forming the obtained mixture into pellets,
b) optionally drying the pellets obtained by step a), and
c) calcining the pellets.

Chrome ore material

[0014] Preferably, the chrome ore material used in step a) contains:

- chrome(III)oxid (Cr_2O_3): 26 to 54 wt%, particularly preferably 40 to 45 wt%,
- aluminum oxide (Al_2O_3): 10 to 30 wt%, particularly preferably 13 to 18 wt%,
- iron(II) oxide (FeO): 12 to 36 wt%, particularly preferably 20 to 28 wt %,
- magnesium oxide (MgO): 9 to 22 wt%, particularly preferably 10 to 15 wt%,
- calcium oxide (CaO): < 5 wt%, particularly preferably < 1 wt%, and
- silicon oxide (SiO_2): 1 to 18 wt%, particularly preferably 2 to 5 wt%.

[0015] The worldwide largest chrome ores deposits are located in South Africa, Zimbabwe, Turkey and the Philippines and in some other countries. The chrome ore is divided into two categories: The metallurgical grade with ≥ 45 wt% of Cr_2O_3 and the chemical grade with < 45% wt% and ≥40 wt% of Cr_2O_3. The largest known deposit of chrome ore is found in Zimbabwe with over 300 million tons.

Chrome Ore Process Residue

[0016] Chrome Ore Process Residue (COPR) sometimes also named chromite ore processing residue is known to person skilled in the art as a waste stream comprising chrome and other metal oxides from the industrial production of chromate. The Chrome Ore Process Residue (COPR) used in step a) is preferably a by-product from the sodium monochromate production process. Therein, chrome ore is mixed with soda ash and heated to a temperature of about 1200°C under oxidizing condition. The reaction mixture is leached with water, and the dried solid residue is the so-called Chrome Ore Process Residue (COPR).
[0017] Preferably, the COPR is obtained in the process for producing sodium monochromate from chromite via an oxidative alkaline digestion with sodium carbonate (no lime process, CaO content of < 5 wt%).
[0018] Preferably, COPR contains metal oxides such as chromium(III) oxide (Cr_2O_3), aluminium oxide (Al_2O_3), iron(III) oxide (Fe_2O_3), iron(II) oxide (FeO), magnesium oxide (MgO), calcium oxide (CaO), silicon oxide (SiO_2), vanadium oxide (V_2O_5), sodium oxide (Na_2O) and sodium monochromate (Na_2CrO_4).
[0019] The Cr(VI) is preferably present as sodium monochromate (Na_2CrO_4) in the COPR.
[0020] The CaO content of the COPR is preferably less than 15 wt%, particularly preferably less than 10 wt%, most preferably less than 5 wt%.
[0021] COPR preferably contains:

- chrome(III) oxide (Cr_2O_3): 7 to 13 wt%, preferably 7.5 to 12.5 wt%,
- aluminum oxide (Al_2O_3): 10 to 30 wt%, preferably 18 to 24 wt%,
- iron(II) oxide (FeO): 36 to 44 wt%, preferably 37 to 42 wt%,
- iron(III) oxide (Fe_2O_3): >0.5% wt%, preferably >2 wt%,
- magnesium oxide (MgO): 9 to 18 wt%, preferably 10 to 17 wt%,
- calcium oxide (CaO): < 10 wt%, preferably < 5 wt%,
- silicon oxide (SiO_2): 0 to 3 wt%, preferably 1 to 3 wt%,
- vanadium oxide (V_2O_5): < 1 wt%, preferably < 0.5 wt%,
- sodium oxide (Na_2O): 0 to 5 wt%, preferably 2 to 5 wt%, and
- sodium monochromate (Na_2CrO_4): 0 to 4.7 wt%, preferably <0.0003 wt%.

[0022] Preferably, the Cr(VI) content of the COPR is 0.01 - 1 wt%.
[0023] Preferably, the Cr content in the COPR is 2 to 25 wt%, particularly preferably 5 to 9 wt%.
[0024] Preferably, the Fe content in the COPR is 28 to 35 wt%, particularly preferably 29 to 34 wt%.
[0025] Preferably, the Si content in the COPR is 0 to 1,5 wt%, particularly preferably 0.4 to 1,0 wt%.
[0026] In an alternative embodiment, the Cr(VI) content of the COPR is preferably < 0.0001 wt%.
[0027] COPR with a Cr(VI) content of < 0.0001 wt% is preferably obtained via a reduction process of COPR with a Cr(VI) content of 0.01 - 1 wt% in that the reduction of Cr(VI) to Cr(III) takes preferably place via polyethylene glycol (PEG) or glycerol as disclosed in WO2014/006196 or, alternatively, in an atmosphere containing less than 0.1% by volume of an oxidizing gas as disclosed in WO 2016074878A1.

Saccharide binder

[0028] The saccharide binder to be used in the present invention can be selected from, monosaccharides, disaccharides, oligosaccharides, and polysaccharides or mixtures thereof, preferably from disaccharides, oligosaccharides, and polysaccharides or mixtures thereof, more preferably from oligosaccharides, and polysaccharides or mixtures thereof and most preferably from polysaccharides and mixtures thereof.
[0029] Examples of monosaccharides are glucose, galactose, fructose and xylose, examples of disaccharides are sucrose, lactose, maltose and trehalose, examples for oligosaccharides include maltodextrins, raffinose, stachyose and fructo-oligosaccharides, examples of polysaccharides are amylose, amylopectin, starch, modified starches, arabinoxylans, chitin glycogen, cellulose, hemicellulose, pectins, hydrocolloids, agarose, dextran and guaran.
[0030] A particularly preferred embodiment of the present invention the saccharide binder comprises guaran, also called guar gum.
[0031] The amount of saccharide binder in the pellets obtained by step a) is typically below 5 wt%, preferably below 4 wt% and most preferably in the range of 1 wt% to 3 wt% based on COPR.
[0032] In further preferable embodiments, the pellets obtained by step a) comprise the saccharide binder in an amount of 0.003 wt% to 1 wt% based on the amount of chrome ore material, COPR, saccharide binder and if present, carbonaceous reductant.

Carbonaceous reductant

[0033] In a preferred embodiment of the present invention, the pellets obtained by step a) comprise less than 3 wt%, preferably less than 2 wt% more preferably less than 1 wt% and most preferably 0 wt% of carbonaceous reductant based on the amount of chrome ore material, COPR, saccharide binder and carbonaceous reductant.
[0034] The term carbonaceous reductant refers to all organic substances, which are capable of reducing the Fe- or Cr oxides in the chrome ore material under the calcining conditions of step c). In particular, said expression refers to the compounds anthracite, char, coke and bituminous coal. For the sake of clarity it is understood in the context of the present invention that the term carbonaceous reductant does not include saccharide binder.
[0035] In an alternative preferred embodiment of the present invention, the pellets obtained by step a) comprise 3 to 25 wt-%, preferably 6 to 20 wt-% of carbonaceous reductant based on the amount of chrome ore material, COPR, saccharide binder and carbonaceous reductant. Said embodiment is particularly useful for the production of metallized calcined, iron- and chrome-containing pellets, which generally includes reduction of at least a part of the pellet's iron- and chrome-oxides into their metallic state during step c).

Pellets

[0036] The term pellets as used in the present invention refers to particular or granular material with regular or irregular shape, preferably with a spheric shape.
[0037] Preferably, the term pellets refers to particles or granules having a volume equivalent to that of a sphere with a diameter of 4-30 mm, more preferably 8-20 mm, most preferably of 10-15 mm.

The process

Step a)

[0038] There are different ways known to the skilled person for mixing the chrome ore material, COPR and an optional carbonaceous reductant before water addition in step a).
[0039] Preferably, the mixing is conducted by using a dry ball mill.
[0040] The solid components used in step a) are preferably milled. The milling can take place prior to the mixing in step a), during the mixing in step a) or after the mixing in step a).
[0041] Preferably, the chrome ore material, COPR, saccharide binder and optionally carbonaceous reductant are milled during mixing in step a).
[0042] In a preferred embodiment, the pellets obtained by step a), comprise:

- 82 to 98.9 wt%, particularly preferably 93 to 98.9 wt% of chrome ore material,
- 0.1 to 15 wt%, particularly preferably 0.1 to 5 wt% of COPR,
- 0.003% to 1wt%, preferably 0.01 to 0.5 wt% and particularly preferably 0.02 to 0.2 wt%, of saccharide binder, and
- 0 to <3 wt%, preferably 0 to 2 wt%, particularly preferably 0 to 1 wt% of carbonaceous reductant,

based on the amount of chrome ore material, COPR, saccharide binder and optional carbonaceous reductant in the pellets.

[0043] In an alternative embodiment, the pellets, obtained by step a), comprise

- 50 to 95 wt%, particularly preferably 75 to 90 wt% of chromite ore material,
- 1 to 15 wt%, particularly preferably 2 to 5 wt% of COPR,
- 0.003% to 1wt%, preferably 0.01 to 0.5 wt% and particularly preferably 0.02 to 0.2 wt%, of saccharide binder, and
- 3 to 25 wt%, preferably 6 to 20 wt% of the carbonaceous reductant,

based on the amount of chrome ore material, COPR, saccharide binder and optional carbonaceous reductant in the pellets.

[0044] Preferably, the mixture obtained after the mixing of the chrome ore material, COPR and optional carbonaceous reductant in step a) provides a particle size distribution (d90) of 50 to 100 μm, particularly preferably of 65 to 85 μm. According to the invention, a d90 of 50 μm means that 90% by volume of the pellets of the mixture have a particle size of 50 μm and below.

[0045] Preferably, the mixture obtained after the mixing of chrome ore material, COPR and an optional carbonaceous reductant is further mixed with water. Thereby, the pelletization takes place. Alternatively, palletization can be effected by pressing the mixture into the desired form.

[0046] The weight ratio of water to the sum of the components chrome ore material, COPR and a carbonaceous reductant is preferably between 1:6 and 1: >100, particularly preferably between 1:8 and 1: >100, most preferably 1: 125.

[0047] The pelletization may take place in either a pan or drum pelletizing unit. Thereby, composite carbon containing (so called "green") pellets are obtained.

[0048] Preferably, the silicon content of the pellets obtained by step a) is below 2.5 wt%, particularly preferably below 2 wt%.

[0049] Preferably, the pellets obtained by step a) do not crack when dropped from a height of up to 0.2 m, particularly preferably of up to 0.4 m, most preferably of up to 0.5 m, on a steel plate. The green wet pellets show, after drying in air, a density higher then pellets produced with a binder state-of-the-art.

Step b)

[0050] The pellets can be pre-dried under ambient conditions, preferably at a temperature of 18 to 30°C, for 4 to 40 hours, preferably for 12 to 30 hours, but this is optional.

[0051] The optional drying is done by heating the pellets under atmospheric conditions, preferably. Particularly preferably, the drying takes place at a temperature above 70°C, most preferably above 100°C. The time for the drying is preferably 2 to 50 hours, particularly preferably 6 to 30 hours, and can be performed in an oven.

Step c)

[0052] The calcining of the pellets obtained by step a) or step b), if step b) is performed, may be conducted in different ways known to the skilled person. This calcining process can be performed either under ambient gas atmosphere or under an atmosphere with reduced oxygen level compared to ambient atmosphere.

[0053] The heating unit is preferably a rotary kiln, a muffle furnace, a tube furnace or a tunnel furnace, preferably a belt tunnel furnace.

[0054] In the heating unit, the wet or optionally dry, pellets obtained by step a) or b) are calcined at oven temperatures of 1250°C to 1600°C, for periods of 1 minute to 8 hours, preferably of 1300°C to 1500°C for periods of 5 minutes to 5 hours.

[0055] Preferably, the inert atmosphere contains less than 0.1 vol-% of oxygen. Particularly preferably, the inert atmosphere is argon.

[0056] In an alternative embodiment of step c) relating to the production of metallized chrome- and iron containing particles, the heating unit is operated as a reduction unit i.e. the heating unit is opreated such as to maintain sufficient reducing conditions in the immediate environment of the particle bed so as to achieve high degrees of both iron and chromium metallisation and commensurately limited degrees of carbon burn-off. In such case, the calcination is preferably carried out at oven temperatures of 1250°C to 1600°C, for periods of 1 to 8 hours, preferably of 1300°C to 1500°C for periods of 2 to 5 hours, in an inert atmosphere.

[0057] Preferably, the inert atmosphere contains less than 0.1 vol-% of oxygen. Particularly preferably, the inert atmosphere is argon.

[0058] The reduction facility is preferably operated in a manner so as to ensure that the preheated pellets are maintained at a temperature of preferably 1350 to 1450°C for a period of between 2 and 5 hours, through the use of an oxygen enhanced coal combustion device. Oxygen support of the combustion device is considered a vital part in ensuring adequate flame geometry and energy release, while enabling the maintenance of a suitably reducing environment in the particle bed to achieve the requisite degree of metallisation.

[0059] The term "metallised particles" means that at least a part of the Fe- and Cr-ions contained in the chromite ore material and the COPR as used in step a) are reduced to chromium and iron in the oxidation state 0. Preferably, the degree of metallisation in the metallised particles obtained by step c) is above 65%, particularly preferably above 75% and most preferably above 85% of the weight of the Fe- and Cr-ions contained in the chromite ore material and the COPR as used in step a).

[0060] The degree of metallisation can be determined via thermographimetric analysis that is known to the skilled person. The loss of weight at those temperatures is directly correlated with the loss of bound oxygen consumed by the reductant component, and therewith the degree of metallisation to Fe and Cr, and the loss of the reductant component itself. After the subtraction of organic compounds in the reductant component, which is determined in a separate measurement with pure reductant component, the degree of metallisation can be calculated with ease.

[0061] By the use of the calcined pellets obtained by step c) the electrical energy consumption for the complete reduction to iron metal and chrome metal in the arc furnace is reduced.

[0062] In both processes the calcined pellets obtained by step c) are discharged, either via direct hot transfer to the smelting furnace or via controlled cooling of the calcined product, to yield cool, mechanically stable pellets.

[0063] In the calcined pellets obtained by step c) the Cr(VI) content is preferably <0.0001 wt%.

[0064] The calcined pellets obtained by step c) provide increased mechanical stability compared to those obtained by step a).

[0065] The calcined pellets can be further stored or transported, e.g. to an electric submerged arc furnace for the preparation of Ferrochrome.

[0066] The calcined pellets obtained by step c) have an average cold crushing strength of at least 130 kgf/pellet, preferably at least 160 kgf/pellet and most preferably at least 200 kgf/pellet. This value is determined in consideration of DIN EN 993-5 (2018) by placing a pellet between two steel plates arranged in parallel. With an hydraulic system, the plates are constantly moved towards each other and the pellet in the gap is squeezed. The applied force is measured continuously. The measurement is stopped, as soon as the applied force decreases while the plates are still moving towards each other (pellet has cracked). The maximum force measured in the described setup is calculated as an applied weight in kgf. 1 kgf are equivalent to 9.806650 N. In the present examples, the cold crushing strength is given the as average of 100 pellets of same size.

Calcined, iron- and chrome-containing pellets and their use

[0067] The present invention further provides calcined, iron- and chrome-containing pellets that contain:

- chrome: 25 to 36 wt%, preferably 28 to 33 wt%,
- iron: 14 to 24% wt%, preferably 15 to 21 wt%, and
- silicon: 0.4 to 2 wt%, preferably 0.4 to 1 wt%,

having a density of >3.35 g/cm^3, preferably >3.40g/cm, more preferably >3.41 g/cm^3.

[0068] The calcined iron- and chrome-containing pellets have an average cold crushing strength of at least 130 kgf/pellet, preferably at least 160 kgf/pellet and most preferably at least 200 kgf/pellet.

[0069] Preferably, the calcined, iron- and chrome-containing pellets contain chrome as chrome(III)oxide (Cr_2O_3) and as chrome metal, iron as iron(II) oxide (FeO) and iron(III) oxide (Fe_2O_3) and as iron metal, and silicon as silicon oxide (SiO_2).

[0070] The ratio of iron metal to iron(II,III) in the calcined, iron- and chrome-containing pellets is preferably <1:2, particularly preferably <1:10.

[0071] The ratio of chrome metal to chrome(III) in the calcined, iron- and chrome-containing pellets is preferably <1:2, particularly preferably <1:10.

[0072] The ratio of iron and chrome metal to iron(II,III) and chrome(III) in the calcined, iron- and chrome-containing pellets is preferably <1:2, particularly preferably <1:10.

[0073] In the calcined, iron- and chrome-containing pellets the Cr(VI) content is preferably <0.0001 wt%. The calcined, iron- and chrome-containing pellets are particularly preferably free of Cr(VI).

[0074] Preferably, the calcined, iron- and chrome-containing pellets have a diameter of 6-13 mm.

[0075] Preferably, the calcined, iron- and chrome-containing pellets according to the invention are obtained by the process for preparing calcined, iron- and chrome-containing pellets according to the invention.

[0076] The invention further provides the use of calcined, iron- and chrome-containing pellets according to the invention for the preparation of Ferrochrome.

[0077] The invention further provides a process for the preparation of Ferrochrome wherein the calcined, iron- and chrome-containing pellets according to the invention are fed into an electric arc furnace and molten under reduction of iron- and chrome oxides.

Mixtures of COPR and saccharide binder and masterbatches

[0078] A further embodiment of the present invention relates to mixtures comprising COPR and saccharide binder wherein the amount of saccharide binder is 0.1 to 5 wt% preferably 0.4 to 4 wt% and most preferably 1 wt% to 3 wt% based on COPR. Said mixtures can comprise up to 30 wt%, preferably up to 20wt% and most preferably up to 10 wt% of further components suitable as additives in the ferrochrome process. Such mixtures can be advantageously used as a precursor for preparing the chrome ore material containing mixtures in the first part of step a).

[0079] A further embodiment of the present invention relates to mixtures comprising COPR and saccharide binder wherein the amount of saccharide binder is more than 5 wt% preferably 5 wt% to 50 wt% and most preferably 5 wt% to 20 wt% based on COPR. Said mixtures can comprise up to 30 wt%, preferably up to 20wt% and most preferably up to 10 wt% of further components suitable as additives in the ferrochrome process. Such mixtures can be advantageously used as masterbatches for preparing the chrome ore material containing mixtures in the first part of step a).

[0080] Typically, the above mentioned mixtures of COPR with saccharide binder are present in a particular form, preferably in a form wherein the extension of the particles in their largest dimension is less than 25 mm, preferably from 0.01 mm to 20 mm and most preferably from 0.1 mm to 15 mm.

[0081] The invention will be described in more detail in the following non-limiting example.

Example A:

[0082] 99.2 parts by weight of chrome ore material (milled in a dry ball mill process down to d90=82μm, type: UG2 chemical grade, origin: Sibanya mine in Waterval Rustenburg, South Africa, moisture 8.7 % by weight), was mixed intensively with 0.8 parts by weight of COPR comprising less than 0.7 ppm of Cr(VI), obtained according to the procedure described in WO2014/006196 and with 0.00247 parts of guar gum.

[0083] The material was placed in a pelletization disc and water was sprayed on the surface while the disc was turning to produce small pellets of about 3mm, which were screened out and used as seed pellets for the actual pelletizing process.

[0084] After the pelletizing process pellets with an diameter of above 11,2 mm were screened out (with 7 wt% of water) and dried. The density of the dried pellets was determined using the displaced volume method.

[0085] Hereafter, the pellets were calcined in a chamber furnace. The temperature was increased rapidly (within few minutes) to 1400°C and hold for 10 minutes. The pellets were then left to cool down to ambient temperature. The density of the indurated pellets was determined on 200 pellets by the volume of displacement method. The cold compression strength (CCS) was determined using 200 indurated pellets produced as above.

Example B (comparative example according to EP18196811.6)

[0086] 99.2 parts by weight of chrome ore material (milled in a dry ball mill process down to d90=82μm, type: UG2 chemical grade, origin: Sibanya mine in Waterval Rustenburg, South Africa, moisture 8.7 wt%), was mixed intensively with 0.8 parts by weight of COPR, received according to procedure described in WO2014/006196.

[0087] The material was placed in a pelletization disc and water was sprayed on the surface while the disc was turning to produce small pellets of about 3mm, which were screened out and used as seed pellets for the actual pelletizing process.

[0088] After the pelletizing process pellets with an diameter of above 11,2 mm were screened out and dried. The density of the dried pellets was determined using the displaced volume method.

[0089] Hereafter, the pellets were calcined in a chamber furnace. The temperature was increased rapidly (within few minutes) to 1400°C and hold for 10 minutes. The pellets were then left to cool down to ambient temperature. The density of the indurated pellets was determined on 200 pellets by the volume of displacement method. The cold compression strength (CCS) was determined using 200 indurated pellets produced as above.

Example C (comparative example according to ZA2004-03429A)

[0090] 99.2 parts by weight of chrome ore material (milled in a dry ball mill process to d90=82μm, type: UG2 chemical grade, origin: Sibanya mine in Waterval Rustenburg, South Africa, moisture 8.7 wt%), was mixed intensively with 0.8 parts by weight of Bentonite MB100S (Supplier: LKAB Sweden, 52 wt% SiO_2, 3 wt% Na_2O, 1 wt% K_2O, 0.4 wt% S, containing 77% Montmorillonite and 6.4 wt% CaO and 10 wt% water).

[0091] The material was placed in a pelletization disc and water was sprayed on the surface while the disc was turning to produce small pellets of about 3mm, which were screened out and used as seed pellets for the actual pelletizing process.

[0092] After the pelletizing process pellets with an diameter of above 11,2 mm were screened out and dried. The density of the dried pellets was determined using the displaced volume method.

[0093] Hereafter, the pellets were calcined in a chamber furnace. The temperature was increased rapidly (within few minutes) to 1400°C and hold for 10 minutes. The pellets were then left to cool down to ambient temperature. The averaged density of the pellets was determined on 200 pellets by volumetric displacement. The cold compression strength (CCS) was determined using 200 indurated pellets produced as above.

[0094] The porosity was calculated based on mass ($M_{Pellets}$), volume ($V_{Pellets}$) and density ($\rho_{Pellets}$) of the pellets, by the following formula:

$$Porosity = \frac{V_{pellet} - {m_{pellet}}/{\rho_{solid\_material}}}{V_{pellet}} \cdot 100$$

Results:

	Example A	**Example B** (comparative)	**Example C** (comparative)
Averaged density of dried pellets (g/cm^3)	**3.24**	**3.30**	**3.09**
Averaged density of calcined pellets (g/cm^3)	**3.41**	**3.45**	**3.34**
Averaged Cold Crush Strength (kgf/pellet)	**>200**	**>120**	**>200**

Claims

1. A process for preparing calcined, iron- and chrome-containing pellets comprising the steps:

   a) mixing chrome ore material, Chrome Ore Process Residue (COPR) and saccharide binder and forming the obtained mixture into pellets,
   b) optionally drying the pellets obtained by step a), and
   c) calcining the pellets.

2. A process according to claim 1, wherein the pellets obtained by step a) comprise less than 3 wt%, preferably less than 2 wt% more preferably less than 1 wt% and most preferably 0 wt% of carbonaceous reductant based on the amount of chrome ore material, COPR, saccharide binder and carbonaceous reductant.

3. A process according to claim 1, wherein the pellets obtained by step a) comprise 3 to 25 wt%, preferably 6 to 20 wt% of the carbonaceous reductant based on the amount of chrome ore material, COPR, saccharide binder and carbonaceous reductant.

4. A process according to any of claims 1 to 3, wherein the pellets obtained by step a) comprise 0.003% to 1wt%, preferably 0.01 to 0.5 wt% and particularly preferably 0.05 to 0.2 wt%, of saccharide binder based on the amount of chrome ore material, COPR, saccharide binder and, if present, carbonaceous reductant.

5. A process according to any of claims 1 to 4, wherein the saccharide binder is selected from glucose, galactose, fructose and xylose, sucrose, lactose, maltose, trehalose, maltodextrins, raffinose, stachyose, fructo-oligosaccharides, amylose, amylopectin, starch, modified starches, arabinoxylans, chitin glycogen, cellulose, hemicellulose, pectins, hydrocolloids, agarose, dextran, guaran and mixtures thereof.

6. A process according to any of claims 1 to 5, wherein the saccharide binder comprises guaran.

7. A process according to any of claims 1 to 6, wherein the COPR contains

- chrome(III) oxide: 7 to 13 wt%, preferably 7.5 to 12.5 wt%,
- aluminum oxide: 10 to 30 wt%, preferably 18 to 24 wt%,
- iron(II) oxide: 36 to 44 wt%, preferably 37 to 42 wt%,
- iron(III) oxide: >0.5% wt%, preferably >2 wt%,
- magnesium oxide: 9 to 18 wt%, preferably 10 to 17 wt%,
- calcium oxide: < 10 wt%, preferably < 5 wt%,
- silicon oxide: 0 to 3 wt%, preferably 1 to 3 wt%,
- vanadium oxide: < 1 wt%, preferably < 0.5 wt%,
- sodium oxide: 0 to 5 wt%, preferably 2 to 5 wt%, and
- sodium monochromate: 0 to 4.7 wt%, preferably <0.0003 wt%.

8. A process according to any of claims 1 to 7, wherein the calcining in step c) is carried out at oven temperatures of 1250°C to 1600°C, for periods of 1 minute to 8 hours, preferably of 1300°C to 1500°C for periods of 5 minutes to 5 hours.

9. A process according to any one of claims 1 to 8 wherein during the calcining step c) a reduction of at least a part of the iron- and chrome oxides in the pellets into their metallic form is achieved.

10. Calcined, iron- and chrome-containing pellets containing:

- chrome: 25 to 36 wt%, preferably 28 to 33 wt%,
- iron: 14 to 24% wt%, preferably 15 to 21 wt%, and
- silicon: 0.4 to 2 wt%, preferably 0.4 to 1 wt%,

having a density of >3.35 g/cm^3 and an average cold crushing strength of at least 130kgf/pellet.

11. Calcined, iron- and chrome-containing pellets according to claim 10 having a density of >3.40g/cm^3, more preferably >3.41 g/cm^3 and an average cold crushing strength of at least 160kgf/pellet, preferably at least 200 kgf/pellet.

12. Use of calcined, iron- and chrome-containing pellets according to any of claims 10 and 11 for the preparation of Ferrochrome.

13. Process for the preparation of Ferrochrome wherein the calcined, iron- and chrome-containing pellets according to any one of claims 10 to 11 are fed into an electric arc furnace and molten under reduction of iron- and chrome oxides.

14. Mixtures comprising COPR and saccharide binder wherein the amount of saccharide binder is 0.1 to 5 wt% preferably 0.4 to 4 wt% and most preferably 1 wt% to 3 wt% based on COPR.

15. Mixtures comprising COPR and saccharide binder wherein the amount of saccharide binder is more than 5 wt% preferably 5 wt% to 50 wt% and most preferably 5 wt% to 20 wt% based on COPR.

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EUROPEAN SEARCH REPORT

Application Number
EP 19 18 3799

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	DWARAPUDI ET AL: "Development of Cold Bonded Chromite Pellets for Ferrochrome Production in Submerged Arc Furnace", ISIJ INTERNATIONAL,, vol. 53, no. 1, 1 January 2013 (2013-01-01), pages 9-17, XP002773408, DOI: 10.2355/ISIJINTERNATIONAL.53.9 * the whole document * -----	1-9	INV. C22B1/24 C22B1/244
Y	CN 106 086 402 A (JIANGSU PROVINCE METALLURGICAL DESIGN INST CO LTD) 9 November 2016 (2016-11-09) * the whole document * -----	1-9	
Y	US 2016/244864 A1 (WINTER FRANK [US]) 25 August 2016 (2016-08-25) * the whole document * -----	1-9	
Y,D	WO 2018/172284 A1 (LANXESS DEUTSCHLAND GMBH [DE]) 27 September 2018 (2018-09-27) * the whole document * -----	1-9	TECHNICAL FIELDS SEARCHED (IPC) C22B

~~The present search report has been drawn up for all claims~~

1

Place of search	Date of completion of the search	Examiner
Munich	27 January 2020	Juhart, Matjaz

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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Application Number

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CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing claims for which payment was due.

☐ Only part of the claims have been paid within the prescribed time limit. The present European search report has been drawn up for those claims for which no payment was due and for those claims for which claims fees have been paid, namely claim(s):

☐ No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for those claims for which no payment was due.

LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

see sheet B

☐ All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.

☐ As all searchable claims could be searched without effort justifying an additional fee, the Search Division did not invite payment of any additional fee.

☐ Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid, namely claims:

☒ None of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims, namely claims:

1-9

☐ The present supplementary European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims (Rule 164 (1) EPC).

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LACK OF UNITY OF INVENTION SHEET B

Application Number
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The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

1. claims: 1-9

   A method for producing pellets

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2. claims: 10-13

   Pellets having cold crushing strength of at least 130 kgf/pellet and density higher than 3.35 g/cm3 , their use and a process for the preparation of ferrochrome by using the pellets.

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3. claims: 14, 15

   A mixture comprising COPR and saccharide

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 19 18 3799

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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27-01-2020

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

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