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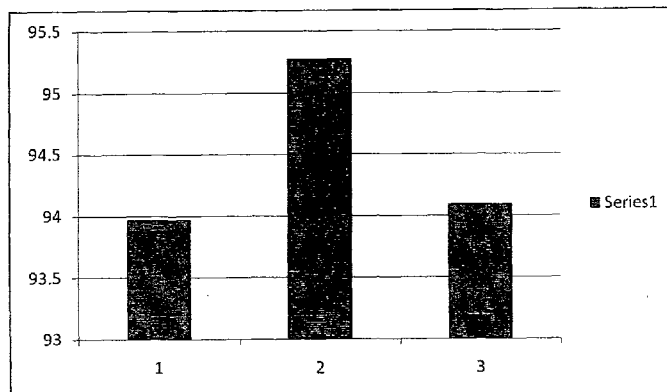
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(54) Title: SINTER PROCESS

Figure 1



(57) Abstract: The invention relates to a process of producing a sintered metal ore, which process comprises sintering a metal ore, a fuel and water in the presence of nanoparticles of a transition metal oxide or a rare earth metal oxide.

SINTER PROCESS

The invention relates to a process of producing a sintered metal ore, a feedstock for sintering and a method of manufacturing a feedstock for sintering. It also concerns the use of nanoparticles of a metal oxide as a combustion improver in the manufacture of sinter for a blast furnace and also the use of the nanoparticles in a feedstock for sintering to improve the efficiency of a sinter process compared to a sinter process using the same feedstock except that it does not contain the nanoparticles of the metal oxide.

The production of metals on an industrial scale, such as iron in quantities up to 12000 tons per day in current modern integrated steelworks, is a complex process engineering problem with chemical reactors incorporating heat and mass transfer on a large scale. For rapid reduction of iron ore in a blast furnace, it is necessary for the iron ore to have a high surface area to volume ratio, which can be achieved by using finely divided particles of ore. However, if finely divided particles of ore were placed into the blast furnace, the high pressure would pack the particles together, restricting the flow of reducing gas through the ore.

In order to provide sinter feedstock that is suitable for rapid reduction in a blast furnace, a sinter plant is used to produce strong (in order to withstand the pressures of the blast furnace), but porous (to allow gas flow around the solid) agglomerates of feed ore and flux. Finely divided particles of ore are fused together to produce a porous, agglomerated sintered product in which the agglomerates have a high surface area to volume ratio in order to maximise the gas/solid reaction interface in the blast furnace. The sintered product provides a metal ore feedstock that is consistent in terms of chemical composition, grain size distribution, reducibility and strength.

Sintering the metal ore before its introduction into the blast furnace also has a number of other associated benefits. Coke used in the sinter process (usually coke fines or breeze) is generally unsuitable for use in the blast furnace, which means that the metallurgical coke used in the blast furnace is not wasted during sintering. The sinter process also heats up the feedstock, which reduces the heat requirement of the blast furnace. Some reduction of the metal ore may also occur during sintering so that less reduction may be required in the blast furnace. Other benefits include the removal of sulphur from sulphur containing metal ores during sintering and the removal of gases, such

as CO₂, SO₂ and H₂O, which would consume carbon if they were present in the blast furnace.

Sintering is typically performed by packing a mixture of finely divided iron ore, flux, and coke onto a bed of a sinter reactor. The top of the packed bed is then ignited and air is sucked through the bed of the reactor. The coke burns with the O₂ in the air and heats the mixture up causing the formation of (CaFeSi)O₄, which melts and binds the particles together. The resulting sinter makes up about 80% of the blast furnace feed. Modern sinter plants are capable of producing up to 25,000 tons of sinter per day. A high quality sintered product is vitally important in ensuring blast furnace efficiency and productivity, and various methods for testing sinter quality have been described, see for example US 5,127,939.

In view of the importance of sintering in the production of metals from a blast furnace, numerous studies have been performed on various aspects of the sinter process. Yavdav et al. (Ironmaking and steelmaking, 29(2), April 2002, 91) looked at the effect of MgO on the sintering characteristics of iron ore. They reported that sintering an iron ore mixture containing increasing amounts of MgO resulted in a deterioration of the sintering rate. However, there was an improvement in the reduction degradation index and softening melting characteristics of the iron ore.

Weidner et al. (US 4,543,121) describe a method for reducing the amount of hydrocarbon gases produced during sintering. The method involves adding an effective amount of a hydrocarbon oxidation catalyst to a mixture of fine iron-containing particles and a combustible carbonaceous material prior to sintering. The oxidation catalyst is a compound containing iron, manganese, cerium, copper, cobalt, chromium, nickel, vanadium or a rare earth metal, such as the naphthenate or octoate salts of these metals. It goes on to mention that the amount of catalyst is not critical, but that enough catalyst must be added to reduce the hydrocarbon vapours produced during sintering. Best results are achieved when the amount of catalyst is between 20 and 100 ppm in the sinter burden.

Hums et al. (US 6,451,250) report a method for reducing the dioxin content in the off-gas from a sinter plant. The method involves admixing, prior to sintering, a material that is catalytically active in decomposing dioxins in the form of fine grains or dust to the material for sintering. Oxides, salts or silicates of a number of metals, which include zinc, nickel, titanium, copper, iron, platinum, vanadium, tungsten, molybdenum, rhenium and

cerium, are mentioned as suitable catalytically active materials. The weight ratio of catalytically active material to the material for sintering is between 1:30 and 1:1.

Paren'kov et al. (Metallurgist, 39(9-10), 1995, 195) describe a method involving the agglomeration and processing of waste of the rare-earth metal industry in blast furnaces, which results in the production of high-quality cast iron. The agglomerated material was Polarit and loparite, which are used as abrasives in the polishing industry. Polarit contains 60% cerium oxide, 24% lanthanum oxide, various iron ores containing iron oxides, manganese oxide and oxides of rare earth metals. The particles of cerium oxide in Polarit are approximately 2 μm in diameter. Loparite contains 31% of oxides of rare earth metals and 38.5% titanium oxide. A fluxed sinter was prepared that contained from 2 to 55% oxides of rare earth metals with Polarit additions of 10, 30 and 50% in order to incorporate a rare earth metal in the iron produced by a blast furnace.

It is known that adding cerium to cast irons opposes graphitization and produces a malleable iron. In steels, cerium degasifies and can help reduce sulphides and oxides. Cerium has also been used in stainless steel as a precipitation hardening agent. It has also been incorporated in alloys that are used to make permanent magnets. Cerium is a major component of ferrocerium (also known as "lighter flint") and, although modern alloys of this type generally use Mischmetal rather than purified cerium, it still is the most prevalent constituent.

Summary of the invention

The invention relates to an improvement in a sinter process for producing sintered ore for a blast furnace. It has surprisingly been found that the rate of sintering of an ore increases when the ore is sintered in the presence of nanoparticles of a metal oxide as described below. The improvement in the rate of sintering affords an increase in the amount of sintered ore produced by the sinter process.

The invention relates to a process of producing a sintered metal ore, which process comprises sintering a metal ore, a fuel and water in the presence of nanoparticles of a metal oxide, wherein a metal of said metal oxide has at least one oxidation state capable of oxidising the fuel during sintering and/or at least one oxidation state capable of being oxidised during sintering.

While not wishing to be bound by the theory above, the invention also relates to a process of producing a sintered metal ore, which process comprises sintering a metal ore, a

fuel and water in the presence of nanoparticles of a transition metal oxide or a rare earth metal oxide.

The process may be used in the production of sinter for use in a blast furnace, where a sintered metal ore is smelted. The metal ore may be a ferrous or non-ferrous metal ore, although the process is particularly suitable for use with ferrous ores. Typically, metal ores that may be sintered include chromite, iron ore, manganese ore and steel plant dust. It is preferred that the metal ore is an iron ore, more preferably the iron ore is an iron oxide ore, such as magnetite, hematite, goethite, limonite or siderite. The metal ores used in the present invention do not generally include a metal oxide used in the invention in nanoparticulate form.

The term “sintering” as used herein refers to a method of bringing about the agglomeration of particles of a metal ore by heating. The agglomeration of the particles of metal ore (and also the reduced metal if some reduction of the metal ore has occurred) usually takes place without melting the particles, but complete or partial melting of the particles during the process is not excluded (i.e. liquid state sintering). The exact sinter process used is not crucial to the practice of the invention. Typically, sintering involves heating the ingredients present in the mixture for sintering to a temperature of at least 650 °C. For some metal ores and metal oxides, the sintering temperature may be lower. The precise temperature will depend on the specific metal ore and the nanoparticles of the metal oxide used in the sinter process.

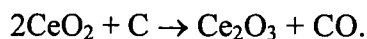
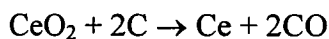
Suitable metal oxides for use in the invention are oxides of transition metals or rare earth metals. Oxides of rare earth metals are preferred. A transition metal as described herein is a member of group 3 (also referred to as group IIIB) to group 12 (also referred to as group IIB) of the Periodic Table. Typically, the transition metal oxide or rare earth metal oxide in the invention is an oxide of zirconium, chromium, vanadium, manganese, iron, lanthanum, cerium, samarium, praseodymium or gadolinium. Preferably, the metal oxide is selected from zirconium, chromium, vanadium, manganese and cerium. Zirconium oxide or cerium oxide are preferred transition metal or rare earth metal oxides. Most preferred is cerium oxide (preferably cerium (IV) oxide). The metal oxide may be a compound where the same metal is present in more than one oxidation state.

The term “metal oxide” as used herein is not intended to encompass the oxide of the metal that is present in the metal ore of the raw materials for sintering, such as iron oxides. The metal oxide present in the metal ore (e.g. iron oxide in an iron ore) is

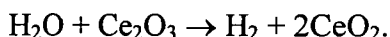
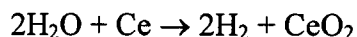
generally not present in nanoparticulate form. In one embodiment, the nanoparticles of the metal oxide are not nanoparticles of iron oxide.

The reactions that are believed to take place during sintering are set out in more detail below, using cerium oxide as an example. Other metal oxides may also be able to catalyse or undergo one or more of the reactions shown in an analogous manner.

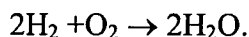
After ignition, the raw materials in the feedstock for sintering heat up and, under these conditions, the cerium oxide oxidises carbon of, or present in, the fuel.



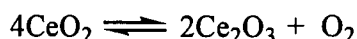
Most of the water present in the sintering mixture or feedstock evaporates during sintering, but a small amount remains because it has no time to evaporate due to the high combustion rate. A residual amount of water oxidises a cerium species to produce hydrogen gas.



The reaction regenerates cerium (IV) oxide, which may then undergo further reaction with carbon present in the fuel and thereby repeat the cycle shown above. The hydrogen produced burns off in the air sucked through the sinter bed and generates additional heat according to the following equation:



The reaction of hydrogen with oxygen proceeds at a high rate and increases the rate of sintering. Oxygen used to react with the hydrogen may also be generated by dissociation of cerium oxide nanoparticles as follows:



Cerium (IV) oxide can become non-stoichiometric in its oxygen content (i.e. it can give up oxygen without decomposing) depending on the ambient partial pressure of oxygen.

Although it will be more usual to employ a simple metal oxide in the invention, it is also possible to use mixed metal oxides. The term mixed metal oxide as used herein refers to a mixture of two or more metal oxides, which will generally be of two or more transition metals and/or rare earth metals.

In one embodiment, the metal oxide is a mixed metal oxide comprising a mixture of at least one transition metal oxide and one rare earth metal oxide.

In another embodiment, the metal oxide is a mixed metal oxide comprising a mixture of at least two different transition metal oxides.

In a further embodiment, the metal oxide is a mixed metal oxide comprising a mixture of at least two different rare earth metal oxides.

When the metal oxide is a mixed metal oxide, at least one metal of the transition metal oxide or rare earth metal oxide typically has at least one oxidation state capable of oxidising the fuel during sintering and/or at least one oxidation state capable of being oxidised during sintering. Preferably, at least two different metals of the mixed metal oxide each independently have at least one oxidation state capable of oxidising the fuel during sintering and/or at least one oxidation state capable of being oxidised during sintering.

Typically, each transition metal oxide of the mixed metal oxide is independently selected from an oxide of zirconium, chromium, vanadium, manganese and iron.

Each rare earth metal oxide of the mixed metal oxide is, typically, independently selected from an oxide of lanthanum, cerium, samarium, praseodymium or gadolinium.

In another embodiment, the metal oxide is a mixed cerium zirconium oxide.

In some instances, the activity or efficiency (e.g. as a catalyst) of the metal oxide, (especially in the case of cerium oxide) can be enhanced by addition of further components in the material.

In an embodiment of the invention, the metal oxide is doped with one or more components that result in additional oxygen vacancies being formed. Thus doping will generally be substitution doping as opposed to interstitial doping. This will clearly enhance the oxygen storage capacity (OSC) of the material, and hence its activity (e.g. its catalytic properties).

Preferably, the host lattice of the doped metal oxide is a transition metal oxide or a rare earth metal oxide. Typically, the host lattice is an oxide of zirconium, chromium, vanadium, manganese, iron, lanthanum, cerium, samarium, praseodymium or gadolinium.

Doping involves the incorporation of a dopant ion component into at least a part of a host lattice of a metal oxide. The metal of the host lattice metal oxide is generally a different element to the dopant ion. Dopant ions can be incorporated singly or in combination of two or three or more.

Such dopant ions are preferably di- or tri-valent in order to provide oxygen vacancies. They must also be of a size that allows incorporation of the ion within the

surface region of the metal oxide nanoparticles. Accordingly metals with a large ionic radius should not be used. For example transition metals in the first and second row of transition metals are generally preferred over those listed in the third.

Typically, the metal oxide (i.e. the host lattice of the metal oxide) is doped with a divalent or trivalent metal, which metal is a rare earth metal, a transition metal, including a noble metal, or a metal of group 2 (also referred to as group IIA), group 3 (also referred to as group IIIB), group 5 (also referred to as group VB) or group 6 (also referred to as group VIB) of the Periodic Table.

In particular, the metal oxide (i.e. the host lattice of the metal oxide) is preferably doped with Zr, Rh, Ni, Cu, Ag, Au, Nb, Ta, Pd, Pt, Fe, Mg, Mn, Cr, Mo, Be, Co, V, Ca, Sr, Ba, Ga, Sn, Si, Al, Pr, Sm, Gd, La or Ce. Preferably, the dopant ion is selected from Mn^{2+} , Mn^{3+} , V^{3+} , V^{5+} and Cr^{3+} . When the dopant ion is a rare earth metal, then the host lattice must be of a size that allows the dopant ion to be incorporated. Thus, it is preferred that the host lattice of the metal oxide is a rare earth metal oxide or is a transition metal oxide, where the transition metal is from the third row of transition metals in the periodic table, when the dopant ion is a rare earth metal.

Typically, the total amount of dopant ion in the host lattice is 0.05 mole% to 10 mole%, preferably 0.1 mole% to 5 mole%, and more preferably 0.5 mole% to 2 mole%.

In an embodiment where the metal oxide is cerium oxide, the cerium oxide serves as an oxygen activation and exchange medium during a redox reaction. When the metal oxide is cerium (IV) oxide then it may be doped with a divalent or trivalent metal which metal is a rare earth metal, a transition metal, including a noble metal, or a metal of group 2 (also referred to as group IIA), group 3 (also referred to as group IIIB), group 5 (also referred to as group VB), or group 6 (also referred to as group VIB) of the Periodic Table. In one embodiment, the oxides will have the formula $\text{Ce}_{1-x}\text{M}'_x\text{O}_2$ where M' is a said metal, in particular Zr, Rh, Ni, Cu, Ag, Au, Nb, Ta, Pd, Pt, Fe, Mg, Mn, Cr, Mo, Be, Co, V, Ca, Sr, Ba, Ga, Sn, Si, Al, Pr, Sm, Gd or La and x has a value up to 0.3, typically 0.01 or 0.1 to 0.2. In another embodiment, the metal oxide has the formula $[(\text{CeO}_2)_{1-n}(\text{REO}_y)_n]_{1-k}\text{M}^*_k$ where M^* is a said metal other than a rare earth metal, RE is a rare earth metal, y is 1 or 1.5 and each of n and k , which may be the same or different, has a value up to 0.5, preferably up to 0.3, typically 0.01 or 0.1 to 0.2. If too much dopant is used, there will be an increasing tendency for it to form an oxyanion thus negating the benefits of introducing it.

Dopants may be incorporated into a metal oxide, such as cerium oxide, using a method as described in WO 03/040270 or WO 2004/065529.

The particles of the metal oxide used in the present invention can be obtained in a conventional manner. Thus, the particles may be prepared by controlled precipitation, combustion synthesis or flame pyrolysis, as well as by other methods described in the literature for the production of nanoparticles.

The reference to nanoparticles as used herein refers to particles having a size of less than one micron. The term nanoparticle refers to a particle distribution where substantially all of the particles (i.e. at least 95%, especially at least 99%, of the particles in a particle distribution) have a size less than one micron.

Generally, it is preferable for the metal oxide nanoparticles to be of a nanocrystalline nature. If the metal oxide is a mixed metal oxide, then it is preferable that the nanoparticles of at least one of the metal oxides present in the mixed metal oxide is nanocrystalline. More preferably, the nanoparticles of each metal oxide of the mixed metal oxide is nanocrystalline.

It is preferred that the average particle size of the nanoparticles does not exceed 1 micron; preferably the nanoparticles of the metal oxide have an average size from 1 to 500 nm, such as from 2 to 300 nm, particularly from 3 to 150 nm, more preferably from 4 to 50 nm, and especially 5 to 20 nm. X-ray diffraction (XRD) has been used to determine the size of the nanoparticles.

The particles may have a regular or an irregular shape. Thus, any reference to particle size as used herein refers to a volume based particle size. The particle size is equal to the size of a sphere having the same volume as that particle. For spherical particles, the diameter of the particle is equal to the diameter of the sphere.

Normally, a distribution of particles having various sizes is obtained. Any reference to particle size, with the exception of the definition for nanoparticles given above, as used herein refers to the size (i.e. the mean particle size) of the particles in a size distribution of the particles. If a nanoparticle of the metal oxide is coated, such as with a coating agent, then the particle size refers to the size of the metal oxide at the core of the coated particle (i.e. it does not include the thickness of the coating).

As the effect of the metal oxide is believed to be surface area dependent, the small particle size renders the nanocrystalline material more effective as a reactant or catalyst. Particles larger than 1 μm may have poor or show no catalytic activity. The metal oxide

particles which are used in the sinter process of the invention should have as large a surface area as possible, such as a surface area of at least $10 \text{ m}^2/\text{g}$ and preferably a surface area of at least 50 or $75 \text{ m}^2/\text{g}$, for example 80 to $150 \text{ m}^2/\text{g}$, or 100 to $300 \text{ m}^2/\text{g}$.

In one embodiment of the invention, the nanoparticles are coated with an organic coating. The organic coating may assist dispersion (e.g. to prevent agglomeration of the nanoparticles) or admixture of the particles into the sinter mix, especially if the metal oxide particles are susceptible to oxidation in air at room temperature. The organic coating is burnt off during sintering.

The nanoparticles are coated with a coating agent that is suitably an organic acid, anhydride or ester or a Lewis base. The coating agent is preferably an organic carboxylic acid or an anhydride, typically one possessing at least 8 carbon atoms, for example 10 to 25 carbon atoms, especially 12 to 18 carbon atoms, such as stearic acid. It will be appreciated that the carbon chain can be saturated or unsaturated, for example ethylenically unsaturated as in oleic acid. Similar comments apply to the anhydrides that can be used. They are preferably dicarboxylic acid anhydrides, especially alkenyl succinic anhydrides, particularly dodecenylsuccinic anhydride, octadecenylsuccinic anhydride and polyisobutenyl succinic anhydride. A preferred anhydride is dodecenylsuccinic anhydride. Other organic acids, anhydrides and esters that can be used in the process of the present invention include those derived from phosphoric acid and sulphonic acid. The esters are typically aliphatic esters, for example alkyl esters derived from an acid and an alcohol, each of which may contain 4 to 18 carbon atoms.

Other coating agents which can be used, although are less preferred, include Lewis bases which possess an aliphatic chain of at least 8 carbon atoms including mercapto compounds, phosphines, phosphine oxides and amines as well as long chain ethers, diols and aldehydes, as well as mixtures of two or more of the coatings mentioned above. The long chain ethers, diols and aldehydes may possess an aliphatic chain of at least 6 carbon atoms, preferably 8 to 18 carbon atoms. The oxygen atom of the long chain ether is bonded to two aliphatic groups, which may be the same (e.g. di-hexyl ether, di-heptyl ether, di-octyl ether) or different (e.g. methyl-octyl ether, ethyl-octyl ether, propyl-octyl ether, iso-propyl-octyl ether). At least one of the aliphatic groups in the long chain ethers has an aliphatic chain may contain at least 6 carbon atoms, preferably 8 to 18 carbon atoms. The other aliphatic chain may have a long chain as defined above, or may contain 1 to 5 carbon atoms.

The coating process can be carried out in an organic solvent. Preferably, the solvent is non-polar and is also preferably non-hydrophilic. It can be an aliphatic or an aromatic solvent. Typical examples include toluene, xylene, petrol, diesel fuel as well as heavier fuel oils. Naturally, the organic solvent used should be selected so that it is compatible with the intended end use of the coated particles.

The coating process generally involves comminuting the particles so as to prevent any agglomerates from forming. Techniques that can be used for this purpose include high-speed stirring or tumbling and the use of a colloid mill, ultrasonics or ball milling. Further details of methods for preparing such coatings can be found in WO 02/092703.

A further aspect of the invention relates to a feedstock or sinter mix for sintering comprising a metal ore, a fuel, nanoparticles of a metal oxide as defined above and optionally a flux. The feedstock may further comprise water, although water may be added to the feedstock prior to sintering. The feedstock may be in the form of a pellet. In pellet form, the raw materials of the feedstock are usually mixed with one another. If the feedstock is in the form of a pellet, then it is preferred that water is present, which aids adhesion or binding of the particles of the raw materials present in the pellet.

The amounts of the materials for sintering are defined below in terms of the amounts for use in the sinter process. If the feedstock comprises all of the materials that are to be sintered, then the amounts of the raw materials described below also correspond to the amounts that are present in the feedstock. However, the feedstock may not comprise all of the materials for sintering and other materials may be added before or after the feedstock has been loaded onto or into the sinter machine or apparatus. Under such circumstances, the feedstock shall comprise an amount of each material that provides the desired amounts of each material for sintering, once the other materials have been added.

The quantity of nanoparticles of a metal oxide used in the invention may vary depending on the metal oxide used. In some cases, the total amount of the metal oxide nanoparticles used in the sinter process of the invention can be from about 0.01 ppm to about 100 ppm by weight, preferably about 0.05 ppm to about 50 ppm by weight based upon the total weight of the raw materials that are present for sintering. These amounts are particularly suitable when the metal oxide is an oxide of cerium, such as cerium (IV) oxide.

Raw materials commonly used in sinter processes for producing sintered products for a blast furnace known in the art may be used in the invention. The metal ore

incorporated in the feedstock may be as defined above. It may be a ferrous or non-ferrous metal ore, but a ferrous ore is preferred. The metal ores that may be incorporated in the feedstock include chromite, iron ore, manganese ore and steel plant dust. It is preferred that the metal ore is an iron ore. It is preferred that the metal ore is an iron ore, more preferably the iron ore is an iron oxide ore, such as magnetite, hematite, goethite, limonite or siderite. Suitable non-ferrous metal ores include ores of lead, copper, and zinc, as well as ores of manganese. The metal ores used in the present invention do not generally include a metal oxide used in the invention in nanoparticulate form.

Iron ore is normally composed of a mixture of FeO and Fe_2O_3 . It may also contain some SiO_2 , Al_2O_3 and/or FeS . The relative amounts will depend on the origin of the ore. A typical iron ore composition is, for example, 45% Fe_2O_3 , 45% Fe_3O_4 ($\text{FeO} \cdot \text{Fe}_2\text{O}_3$) and 10% SiO_2 . The feedstock may also, for example, include iron-containing waste and returned ore that has already been sintered. The feedstock may also comprise steel plant dust, in addition to the metal ore.

Generally, the metal ore will be finely divided or crushed into lumps having an average particle size of from 1 to 20 mm, more typically 1 to 12 mm in size, more preferably 2 to 8 mm in size. The metal ore usually makes up from 20% to 70% by weight, particularly 25% to 60% by weight, more preferably 30% to 50% by weight, of the raw materials for the sinter process of the invention. Typically, the flux is finely divided or crushed into lumps and has a similar average particle size to the metal ore. It is preferred that the average particle size of the flux is from 1 to 20 mm, more typically 1 to 12 mm in size, more preferably 2 to 8 mm in size.

It is preferred that a flux is sintered with the metal ore, the fuel, water and nanoparticles of the metal oxide. The flux typically comprises CaO , CaCO_3 , MgO , a mixture thereof, or a mixture of one of these with SiO_2 , usually in the form of limestone, dolomite, olivine or serpentine. Normally, limestone (CaCO_3) and/or lime (CaO) is added to achieve a lime and/or limestone to silica molar ratio of around 1. A flux is added to remove the waste material from the molten metal by formation of a slag. The amount of flux commonly used in the invention is from 5% to 25% by weight, preferably from 7% to 20% by weight, more preferably from 10% to 15% by weight, of the raw materials used in the sinter process of the invention.

Typically, the fuel is a solid, carbonaceous fuel, such as coal, coke or mixtures thereof. It is preferred that the fuel is coke. The solid fuel generally has an average

particle size not exceeding 5 mm, preferably the average particle size is from 0.5 mm to 3 mm.

Generally, the fuel is present in an amount of 1 to 15% by weight, preferably 2 to 10% by weight, more preferably 3 to 6% by weight, of the raw materials used in the sinter process of the invention. The fuel usually makes up 12 to 20% by volume of a mixture of raw materials for sintering.

Water is also present in the sinter process. It is normally added to the feedstock prior to or during the initial stages of sintering to impart strength (by capillary adhesion of the particles) and to provide optimum permeability of the mixture of raw materials for reduced electricity consumption. It may also be added to raw materials that have already been loaded onto or into the apparatus for performing the sinter process. Water is present in an amount of 1% to 20% by weight, preferably 3% to 15% by weight, more preferably 5% to 10% by weight, of the raw materials for sintering in the sinter process of the invention.

A convenient way of adding the metal oxide nanoparticles to the other raw materials for sintering is as a water dispersion of the metal oxide nanoparticles. In such dispersions, the concentration of the metal oxide in the dispersion is from about 5 ppm by weight to about 200 ppm by weight, preferably from about 10 ppm by weight to about 100 ppm by weight, more preferably from about 20 ppm up to about 80 ppm by weight of metal oxide nanoparticles, e.g. about 40 ppm by weight of metal oxide nanoparticles, such as cerium oxide nanoparticles.

A proportion of the metal ore, fuel and flux used in the invention may be return sinter. Return sinter may contribute up to 50% by weight. Return sinter is processed material that was unsuitable for the blast furnace. Around a third of it is usually warm sinter that has just been processed, the rest being cold.

Other materials may also be included in the feedstock or with the raw materials in the process of the invention. A binder, such as bentonite, cement, cement clinker or mixtures thereof, may be present. Flue dust, which is the dust that is emitted with the exhaust gas from the top of the blast furnace, may also be added.

The process of the invention for producing a sintered metal ore is not limited to any particular method. A commonly used method employs a sintering machine incorporating a travelling grate. The machine may have a hearth area from 0.5 m to 7 m in width by 50 m to 150 m long. Typically, the hearth width is 2m to 5m. The length of the hearth is 75 m

to 120 m. The raw materials for sintering or the feedstock are loaded onto a pallet or bed of the sintering machine, usually to a predetermined height, such as a thickness of 400 to 600 mm. The materials move along the sinter bed of the sintering machine, usually on a pallet that moves along a track, while sintering is performed. After sintering, the resulting sinter cake may be passed under a plate for settling the materials, the bottom edge of which will level off the sinter cake, and/or a sinter breaker (e.g. a roller with spikes driving through a multiplicity of stationary bars) to break the sintered product into lumps to aid cooling.

The metal oxide of the invention may be loaded onto the pallet at the same time as the other materials, or may be loaded separately either before or after the other materials. Similarly, water may also be added at the same time as the other materials, or may be added separately either before or after some or all of the other materials have been loaded.

In one embodiment, the raw materials of the feedstock or the raw materials loaded onto the pallet are mixed with one another. In another embodiment, the raw materials are loaded onto the pallet in layers. The layers may be arranged by particle size of the raw materials or by the chemical identity of the raw material.

A convenient way of adding both the metal oxide and the water to the other raw materials that have been loaded onto the pallet is as a water dispersion of the metal oxide nanoparticles. The water dispersion may be applied to the other raw materials in a variety of manners, but a particularly convenient method is to spray the dispersion onto the loaded material.

Once the metal ore, fuel, metal oxide nanoparticles, water and optionally a flux have been loaded onto the pallet, then the solid fuel at top of the loaded pallet is ignited. After ignition, burning of the solid fuel is continued while air is sucked downward. The gas passes through the bed generating a pulse of hot gas and the heat this produces is sufficient to sinter the raw materials, which will eventually produce a sintered product or sinter cake. The heat usually reaches temperatures up to about 1200 °C. As the pulse moves further down the bed, it is followed by cooler air which causes solidification that binds the particles together. In general the heat pulse will take in the order of 15 minutes to pass through the bed. As a result, extremely long travelling grates are required, sinter beds being in the order of 50m long.

A further aspect of the invention relates to a method of manufacturing a feedstock for sintering. A feedstock of the invention may be prepared using standard techniques

known in the art. However, the method described herein is a convenient method of preparing the feedstock. The method of manufacturing a feedstock for sintering, comprises admixing a metal ore, a fuel, nanoparticles of a metal oxide as described above and optionally a flux.

The raw materials may be admixed, in any order, in a drum or other suitable mixing apparatus and may form a granulated feedstock. The mixed or granulated feedstock may then be pelletised using a pelletising machine or other similar apparatus. Other materials described above, such as a binder, may also be added. Water may be added to the drum to aid binding of the ingredients.

In one embodiment, the nanoparticles of the metal oxide are dispersed in a solvent. The solvent may be water or an organic, hydrocarbon solvent, such as petrol, diesel, pentane or hexane. If the metal oxide is dispersed in an organic, hydrocarbon solvent, then the solvent will combust during sintering. The combustion of the solvent may aid the sintering process.

It is preferred that the nanoparticles of the metal oxide are dispersed in water. The nanoparticles of the metal oxide may have a coating as described above, which may aid dispersion of the nanoparticles in the solvent or prevent them from degrading before sintering. One convenient method of producing a dispersion of the nanoparticles of the metal oxide is to dilute a concentrated aqueous dispersion of the metal oxide nanoparticles with water that contains, for example, from about 10% by weight up to about 35% by weight of metal oxide nanoparticles, for example about 30% by weight of metal oxide nanoparticles, such as cerium oxide nanoparticles. Such a concentrated aqueous dispersion may be charge stabilised by addition, for example, of an acid, such as nitric acid (to a pH of about 1) or, more preferably, acetic acid (to a pH of about 3).

In the invention, the required amount of water or the water dispersion of metal oxide nanoparticles can be added in predetermined ratios by means of spray nozzles. An organic solvent dispersion of the metal oxide nanoparticles can be added to the feedstock or applied directly to a sinter bed by spraying.

The invention also relates to uses of nanoparticles of a metal oxide as defined herein. A first use is the use of nanoparticles of a metal oxide as described above as a combustion improver in the manufacture of sinter for a blast furnace. Typically, one of the benefits of using the nanoparticles of the metal oxide as a combustion improver is that the nanoparticles reduce the consumption of fuel during sintering. Thus, the invention also

relates to the use of nanoparticles of the metal oxide to reduce the consumption of fuel, preferably coke, in the manufacture of sinter for a blast furnace compared to a sinter process when the same feedstock is sintered in the absence of the nanoparticles of the metal oxide under substantially the same conditions. The term “substantially” used in this context refers to sintering conditions that are, for all practical purposes, the same (i.e. any differences in the sintering conditions, such as the sintering temperature, pressure, amount of material to be sintered etc, are minor and would not alter the yield of sinter by more than 0.1%).

A second use is the use of nanoparticles of a metal oxide in a feedstock for sintering to improve the efficiency of a sinter process compared to a sinter process using the same feedstock except that it does not contain the nanoparticles of the metal oxide. The improvement in efficiency is the sinter speed of the process and/or the productivity of the process (i.e. amount of sintered product produced in a given time).

Brief description of drawings

Figure 1 is a histogram showing the output capacity of sinter during a Base period (1), a Trial period (2) and a Monitoring period (3), as shown on the x-axis. The amount of sinter output is represent on the y-axis in tons per hour.

Figure 2 is a histogram shows the % amount of coke consumption in a sinter furnace burden (on the y-axis) after sintering during a Base period (1), a Trial period (2) and a Monitoring period (3) (shown on the x-axis).

Examples

The invention will now be illustrated by the following, non-limiting Examples.

Example 1

Sinter process trials were carried out using a 430 mm sinter pot fitted with an exhaust fan having the following specification:

Rotor speed (rpm)	2900
Suction discharge (kPa)	16
Capacity (m ³ /min)	100

The composition of the sintering mixture is shown in Table 1 below.

Ingredient	Amount (% weight)
Coke fines	4.2
Return sinter	30.0
Limestone	9.36
Water dispersion of cerium oxide	7.5
Ore mixture	48.94

Table 1

The composition of the ore mixture listed in Table 1 above is shown in Table 2 below.

Ingredient	Amount (% weight)
Iron ore concentrate	67.1
Sintering ore	20.2
Iron-bearing waste	9.9
Lime	2.8

Table 2

The sintering mixture in Table 1 was sintered on a sinter bed using different concentrations of cerium oxide in the water dispersion, which was obtained by adding a 2% by weight cerium oxide dispersion to water. The results are shown below.

	Ratio by weight of 2% by weight cerium oxide dispersion:water					
	0	1:250	1:500	1:1000	1:2000	1:2500
Vertical sintering speed, mm/min	18.18	18.74	19.49	18.55	18.21	18.19
Specific productivity (> 5mm), tonne/(m ² hour)	1.511	1.603	1.634	1.520	1.525	1.512

Table 3

Application of a water dispersion of cerium oxide to the sintering mixture at a ratio of 1:500 (2% cerium oxide dispersion:water) by weight, i.e. a water dispersion containing 40

ppm by weight cerium oxide, increased productivity by 8.14% in comparison to the standard process where no cerium oxide was present.

Example 2

The 2% cerium oxide dispersion of nanoparticles in Example 1 was replaced by a 30% by weight cerium oxide dispersion of nanoparticles (which has been charge stabilised by addition of acetic acid and has a pH of about 3). The cerium oxide dispersion was added to water to provide a concentration of the dispersion to water in a ratio of 1:7500. The resulting mixture was then used to water the sinter burden. The industrial trials were carried out at a sinter plant. During the trial, sintering was carried out over three periods:

1. Base period over 9 months without any cerium oxide present.
2. Trial period over 19 days when cerium oxide was added to the sinter burden. The content of fine concentrates in the sinter burden was 60-67%.
3. Monitoring period over 6 days without any cerium oxide present. The content of fine concentrates in the sinter burden was 64-67%.

The results of the trials are set out in Tables 4 and 5 below. The output capacity of the sinter plant when using cerium oxide increased producing 95.09 tons per hour, compared to 93.97 tons per hour during the Base period (1) and 94.09 tons per hour during the Monitoring period (3). These results are illustrated in Figure 1.

There was 1.38% relative improvement in output performance compared to the Base period (1) and a 1.25% relative improvement compared to the Monitoring period (3). It was also possible to operate the sinter machine at a higher velocity when using cerium oxide without deteriorating sinter quality.

During the Trial period (2), coke consumption in the furnace burden was less (see Figure 2) than either the Base period (1) or the Monitoring period (3).

Parameter		Capacity (ton/hr)	Sinter machine velocity (m/min)	Height of batch layer (mm)	Coke consumption in sinter furnace burden (%)	Returns consumption in furnace burden (%)	Total output of sinter returns((%)	Temperature of the stabilized agglomerate (°C)
Period	Base (1)	93.97	1.89	268	3.21	30.72	33.85	74.4
	Trial (2)	95.27	1.95	280	3.13	27.32	31.00	100.45
	Monitoring (3)	94.09	1.96	280	3.38	27.88	32.03	103.33
Comparison with Trial (2)	Base (1)	Rel	+3.17	+4.48	-2.49	-11.07	-8.42	+35.01
		Abs	+0.06	+12	-0.08	-3.4	-2.85	+26.05
	Monitoring (3)	Rel	-0.51	0.0	-7.40	-2.01	-3.22	-2.79
		Abs	-0.01	0.0	-0.25	-0.56	-1.03	-2.88

Table 4

Parameter		% Fraction of 0 to 5 mm content (sinter plant sizing)	% Fraction 0 to 5 mm content (blast furnace plant sizing)	% Drum blow abrasion	
Period	Base (1)	-	7.60	67.61 4.67	
	Trial (2)	7.65	8.56	68.27 5.03	
	Monitoring (3)	7.43	8.46	67.31 4.62	
Comparison with Trial (2)	Base (1)	Rel	-	+12.63	+0.98 +7.71
		Abs	-	+0.96	+0.66 +0.36
	Monitoring (3)	Rel	+2.96	+1.18	+1.43 +8.87
		Abs	+0.22	+0.1	+0.96 +0.41

Table 5

CLAIMS

1. A process of producing a sintered metal ore, which process comprises sintering a metal ore, a fuel and water in the presence of nanoparticles of a metal oxide, wherein a metal of said metal oxide has at least one oxidation state capable of oxidising the fuel during sintering and/or at least one oxidation state capable of being oxidised during sintering.
2. A process according to claim 1, wherein said metal oxide is a transition metal oxide or a rare earth metal oxide.
3. A process of producing a sintered metal ore, which process comprises sintering a metal ore, a fuel and water in the presence of nanoparticles of a transition metal oxide or a rare earth metal oxide.
4. A process according to either claim 2 or 3, wherein the metal oxide is an oxide of zirconium, chromium, vanadium, manganese, iron, lanthanum, cerium, samarium, praseodymium or gadolinium.
5. A process according to any one of the preceding claims wherein the metal oxide is doped or is a mixed metal oxide.
6. A process according to claim 4 wherein the metal oxide is cerium oxide, which cerium oxide is optionally doped.
7. A process according to any one of the preceding claims, wherein the nanoparticles of the metal oxide have an average particle size from 1 to 500 nm, such as from 2 to 300 nm, particularly from 3 to 150 nm, more preferably from 4 to 50 nm, and especially 5 to 20 nm.
8. A process according to any one of the preceding claims, wherein the metal oxide is present in a total amount of from about 0.01 ppm to about 100 ppm by weight, preferably

about 0.05 ppm to about 50 ppm by weight based upon the total weight of the raw materials that are present for sintering.

9. A process according to any one of the preceding claims, wherein the metal ore is an iron ore.
10. A process according to any one of the preceding claims, which process comprises sintering a flux with the metal ore, the fuel, water and the nanoparticles of a metal oxide.
11. A process according to any one of the preceding claims, wherein the fuel is a solid, carbonaceous fuel, preferably coal, coke or mixtures thereof.
12. A process according to any one of the preceding claims, wherein water is present in an amount of 1% to 20% by weight of the raw materials for sintering, preferably 2% to 10% by weight, more preferably 3% to 6% by weight.
13. A process according to any one of the preceding claims, wherein the nanoparticles of the metal oxide are added, preferably by spraying, to the metal ore, the fuel and optionally the flux as a dispersion in water, preferably containing about 5 ppm by weight to about 200 ppm by weight, preferably from about 10 ppm by weight to about 100 ppm by weight, more preferably from about 20 ppm up to about 80 ppm by weight of metal oxide nanoparticles, e.g. about 40 ppm by weight of metal oxide nanoparticles, such as cerium oxide nanoparticles.
14. A process according to any one of the preceding claims, wherein the metal ore, fuel, water, nanoparticles of the metal oxide and optionally the flux are present as a mixture with a binder.
15. A process according to any one of the preceding claims, wherein the metal ore, the fuel, the nanoparticles of the metal oxide and optionally the flux are in the form of a pellet, and the pellet is loaded onto a sintering machine before sintering.

16. A process according to any one of the preceding claims, wherein the metal ore, the fuel, optionally the nanoparticles of the metal oxide and optionally the flux are loaded onto a sintering machine, preferably to a predetermined height, preferably to a thickness of about 400 to 600 mm, before sintering.
17. A process according to claim 16, wherein water is added before sintering to the metal ore, the fuel, optionally the nanoparticles of the metal oxide and optionally the flux after they have been loaded onto a sintering machine, preferably the water is added by spraying.
18. A feedstock for sintering comprising a metal ore, a fuel, nanoparticles of a metal oxide and optionally a flux, wherein a metal of said metal oxide has at least one oxidation state capable of oxidising the fuel during sintering and/or at least one oxidation state capable of being oxidised during sintering.
19. A feedstock according to claim 18, wherein said metal oxide is a transition metal oxide or a rare earth metal oxide.
20. A feedstock for sintering comprising a metal ore, a fuel, nanoparticles of a transition metal oxide or a rare earth metal oxide, and optionally a flux.
21. A feedstock according to any one of claims 18 to 20, wherein the metal oxide is an oxide of zirconium, chromium, vanadium, manganese, iron, lanthanum, cerium, samarium, praseodymium or gadolinium.
22. A feedstock according to any one of claims 18 to 21 wherein the metal oxide is doped or is a mixed metal oxide.
23. A feedstock according to claim 21, wherein the metal oxide is cerium oxide, which cerium oxide is optionally doped.

24. A feedstock according to any one of claims 18 to 23, wherein the nanoparticles of the metal oxide have an average particle size from 1 to 500 nm, such as from 2 to 300 nm, particularly from 3 to 150 nm, more preferably from 4 to 50 nm, and especially 5 to 20 nm.

25. A feedstock according to any one of claims 18 to 24, wherein the amount of metal oxide present in the feedstock provides from about 0.01 ppm to about 100 ppm by weight, preferably about 0.05 ppm to about 50 ppm by weight based upon the total weight of the raw materials that are present for sintering.

26. A feedstock according to any one of claims 18 to 25, wherein the metal ore is an iron ore.

27. A feedstock according to any one of claims 18 to 26, which comprises a flux.

28. A feedstock according to any one of claims 18 to 27, wherein the fuel is a solid, carbonaceous fuel, preferably coal, coke or mixtures thereof.

29. A feedstock according to any one of claims 18 to 28 further comprising water.

30. A feedstock according to claim 29 wherein the amount of water present in the feedstock provides 1% to 20% by weight of the materials for sintering, preferably 2% to 10% by weight, more preferably 3% to 6% by weight.

31. A feedstock according to any one of claims 18 to 30, wherein the feedstock further comprises water and wherein the amount of nanoparticles of the metal oxide in the feedstock corresponds to from about 5 ppm by weight to about 200 ppm by weight, preferably from about 10 ppm by weight to about 100 ppm by weight, more preferably from about 20 ppm up to about 80 ppm by weight of metal oxide nanoparticles, e.g. about 40 ppm by weight of metal oxide nanoparticles, such as cerium oxide nanoparticles of the added water.

32. A feedstock according to any one of claims 18 to 31 further comprising a binder.

33. A feedstock according to any one of claims 18 to 32 in the form of a pellet.
34. A method of manufacturing a feedstock for sintering, comprising admixing a metal ore, a fuel, nanoparticles of a metal oxide and optionally a flux, wherein a metal of said metal oxide has at least one oxidation state capable of oxidising the fuel during sintering and/or at least one oxidation state capable of being oxidised during sintering.
35. A method according to claim 34, wherein said metal oxide is a transition metal oxide or a rare earth metal oxide.
36. A method of manufacturing a feedstock for sintering, comprising admixing a metal ore, a fuel, nanoparticles of a transition metal oxide or a rare earth metal oxide, and optionally a flux.
37. A method according to any one of claims 34 to 36, wherein the metal oxide is an oxide of zirconium, chromium, vanadium, manganese, iron, lanthanum, cerium, samarium, praseodymium or gadolinium.
38. A method according to any one of claims 34 to 37 wherein the metal oxide is doped or is a mixed metal oxide.
39. A method according to claim 37, wherein the metal oxide is cerium oxide, which cerium oxide is optionally doped.
40. A method according to any one of claims 34 to 39, wherein the nanoparticles of the metal oxide have an average particle size from 1 to 500 nm, such as from 2 to 300 nm, particularly from 3 to 150 nm, more preferably from 4 to 50 nm, and especially 5 to 20 nm.
41. A method according to any one of claims 34 to 40, wherein the amount of metal oxide admixed to manufacture the feedstock provides from about 0.01 ppm to about 100 ppm by weight, preferably about 0.05 ppm to about 50 ppm by weight based upon the total weight of the raw materials that are present for sintering.

42. A method according to any one of claims 34 to 41, wherein the metal ore is an iron ore.
43. A method according to any one of claims 34 to 42, which comprises the step of admixing a flux.
44. A method according to any one of claims 34 to 43, wherein the fuel is a solid, carbonaceous fuel, preferably coal, coke or mixtures thereof.
45. A method according to any one of claims 34 to 44 further comprising the step of admixing water.
46. A method according to claim 45, wherein the amount of water admixed in the manufacture of the feedstock provides 1% to 20% by weight of the materials for sintering, preferably 2% to 10% by weight, more preferably 3% to 6% by weight.
47. A method according to claim 45 or claim 46, wherein the amount of nanoparticles of the metal oxide admixed in the manufacture of the feedstock provides from about 10 ppm by weight up to about 200 ppm by weight of metal oxide nanoparticles, preferably from about 20 ppm up to about 80 ppm by weight of metal oxide nanoparticles, such as cerium oxide nanoparticles, of the added water.
48. A method according to any one of claims 34 to 47 further comprising the step of admixing a binder.
49. A method according to any one of claims 34 to 48, comprising the step of admixing a water dispersion of the nanoparticles of the metal oxide in the manufacture of the feedstock.
50. A method according to any one of claims 34 to 48, comprising the step of admixing an organic, hydrocarbon solvent dispersion of the nanoparticles of the metal oxide in the manufacture of the feedstock.

51. A method according to any one of claims 34 to 50, further comprising the step of pelletising the feedstock.
52. Use of nanoparticles of a metal oxide as a combustion improver in the manufacture of sinter for a blast furnace, wherein a metal of said metal oxide has at least one oxidation state capable of oxidising the fuel during sintering and/or at least one oxidation state capable of being oxidised during sintering.
53. Use of nanoparticles of a transition metal oxide or a rare earth metal oxide as a combustion improver in the manufacture of sinter for a blast furnace.
54. Use of nanoparticles of a metal oxide in a feedstock for sintering to improve the efficiency of a sinter process compared to a sinter process using the same feedstock except that it does not contain the nanoparticles of the metal oxide, wherein a metal of said metal oxide has at least one oxidation state capable of oxidising the fuel during sintering and/or at least one oxidation state capable of being oxidised during sintering.
55. Use of nanoparticles of a transition metal oxide or a rare earth metal oxide in a feedstock for sintering to improve the efficiency of a sinter process compared to a sinter process using the same feedstock except that it does not contain the nanoparticles of the transition metal oxide or the rare earth metal oxide.
56. Use according to claim 52 or claim 54, wherein said metal oxide is a transition metal oxide or a rare earth metal oxide.
57. Use according to any one of claims 52 to 56, wherein the metal oxide is an oxide of zirconium, chromium, vanadium, manganese, iron, lanthanum, cerium, samarium, praseodymium or gadolinium.
58. Use according to any one of claims 52 to 57 wherein the metal oxide is doped or is a mixed metal oxide.

59. Use according to claim 57, wherein the metal oxide is cerium oxide, which cerium oxide is optionally doped.

60. Use according to any one of claims 52 to 59, wherein the nanoparticles of the metal oxide have an average particle size from 1 to 500 nm, such as from 2 to 300 nm, particularly from 3 to 150 nm, more preferably from 4 to 50 nm, and especially 5 to 20 nm.

61. Use according to claim 54 or claim 55, or any one of claims 56 to 60 when dependent on either claim 54 or claim 55, wherein the improvement in efficiency is the sinter speed of the process and/or the productivity of the process.

62. A process, a feedstock, a method of manufacturing a feedstock and uses substantially as described herein with reference to the Examples.

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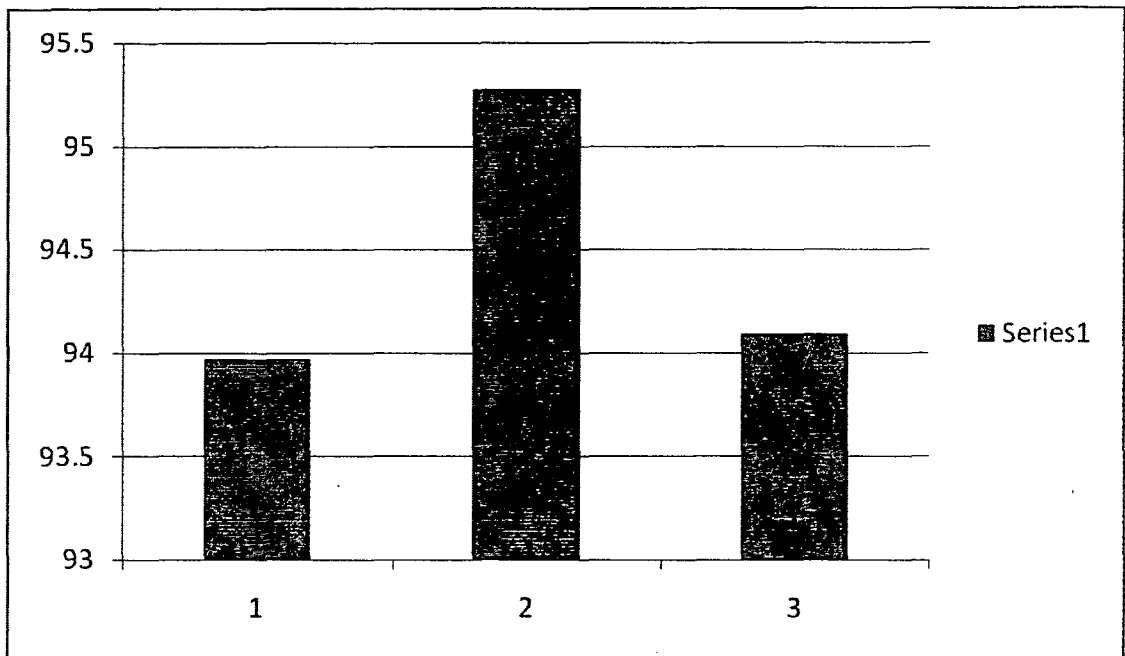


Figure 1

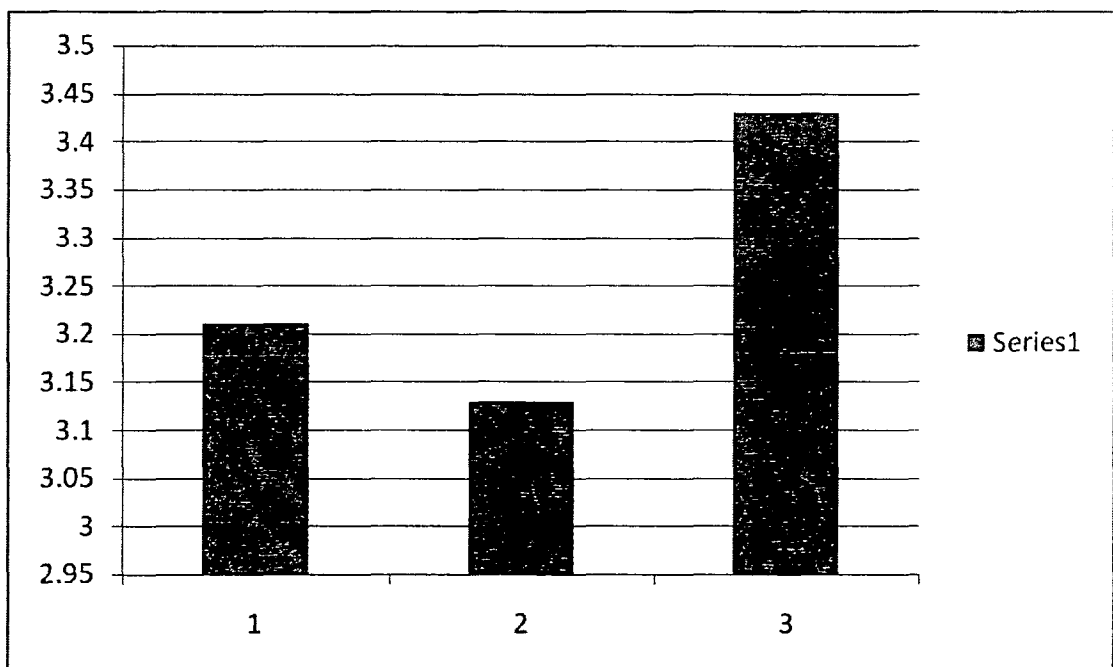


Figure 2