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(54) Title: METHOD FOR PRODUCING MANGANESE ORE PELLETS

(57) Abstract: The invention relates to a method for producing sintered manganese ore pellets. The method comprises producing a pelletizing feed comprising finely divided manganese ore and binding agent; pelletizing the pelletizing feed to produce green pellets; and sintering the green pellets in a steel belt sintering furnace. The sintering step comprises conveying the pellets on a steel belt through process zones of different temperatures, the process zones including at least one drying zone, at least one heating zone, at least one sintering zone, and at least one cooling zone, preferably three.



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METHOD FOR PRODUCING MANGANESE ORE PELLETS**FIELD OF THE INVENTION**

The invention relates to a method for producing sintered manganese ore pellets. The invention also relates to sintered manganese ore pellets prepared by said method.

BACKGROUND OF THE INVENTION

Remarkable amounts of finely divided ore particles are obtained in connection with mining, crushing, transport and handling of manganese ore. Finely divided manganese ore having a grain size below 6-9 mm cannot be directly used in manganese alloy smelting. Finely divided ore easily forms covers and crusts on top of the charge in an electric furnace. Crust formation can cause gas eruptions, problems in the settling of the charge and extensive disturbances in the smelting operation.

Manganese ore fines are typically agglomerated and sintered with a travelling grate sintering apparatus, when large production of manganese ore sinter is needed. The amount of coke used in sintering is substantial, even as high as 10 w-%, because manganese ore fines are mainly melted in the sintering process. The product - sintered manganese ore - is then crushed to a particle size below 50-75 mm. The product is porous, hard and sharp. The crushed product with a particle size of 6-75 mm is fed to a smelting furnace. Fine fraction created in the handling of the product is re-circulated back to the agglomeration unit and sintering furnace. The re-circulation load can be as high as 15-20% of the sintered product. Re-circulation of such a huge percentage increases the energy costs of the sintering process.

US 6063160 discloses a method for sintering finely divided manganese-containing material having a particle size smaller than 6 mm in a conveyor-type sintering apparatus in an essentially continuous operation. The process comprises the steps of adding a binding agent and an optional carbon-bearing material to the finely-divided material, micro-pelletizing the resulting mixture, and passing the micro-pelletized composition through a drying and preheating zone, a reaction and sintering zone, and a cooling zone. The sintered material is crushed, screened and conveyed to a smelting plant. The sinter thus produced lacks mechanical resistance to endure excessive handling and long-distance hauling.

Another manganese pellet production process of the prior art uses manganese ore which has been calcinated in a fluidized bed in a reducing atmosphere. The process involves thermal treatment, also known as calcination, of manganese ore, followed by pelletizing and sintering. The calcination aims at generating magnetite and facilitating elimination of iron through magnetic separation, leading to manganese ore enrichment. A side effect of thermal treatment is decomposing of manganese superior oxides which interfere with manganese pellet burning in traditional production processes.

WO 2010/009527 A1 discloses a process to produce manganese pellets from non-calcinated manganese ore. The process comprises ore size preparation, flux addition, agglomerant (binding agent) addition, pelletizing resulting in crude pellets, and thermal processing through drying, pre-heating and heating the crude pellets.

In smelting sintered pellets are preferred over sinter due to their higher porosity, uniform size and uniform shape.

Although important for steelmaking, production of manganese ore pellets has not been satisfactorily solved so far. It is difficult to obtain physically adequate manganese pellets from manganese ore. A
5 physically inadequate pellet may generate excessive fines when handled, in hauling, and during in-furnace reduction. The generation of fines may lead to product loss or poor material performance during reduction due to loss of bed permeability.

10

OBJECTIVE OF THE INVENTION

An object of the invention is to provide a new and improved process for manufacturing sintered manganese pellets. Another object of the invention is
15 to provide manganese ore pellets suitable for the production of stainless steel in an easy to use form.

SUMMARY OF THE INVENTION

The method according to the present invention
20 is characterized by what is presented in claim 1.

More precisely, the method comprises producing a pelletizing feed comprising finely divided manganese ore and binding agent; pelletizing the pelletizing feed to produce green pellets; and sinter-
25 ing the green pellets in a steel belt sintering furnace, the sintering step comprising conveying the pellets on a steel belt through process zones of different temperatures, the process zones including at least one drying zone, at least one heating zone, at least
30 one sintering zone, and at least one cooling zone, preferably three.

In one embodiment of the present invention, finely divided manganese ore is produced by wet grinding and filtering manganese ore fines.

In another embodiment of the present invention, finely divided manganese ore is produced by dry grinding manganese ore fines.

In one embodiment of the present invention,
5 the method comprises grinding and screening the manganese ore to produce a particle size distribution comprising less than 50% below 400 mesh (38 μm) and 40-85%, more preferably 55-70% below 200 mesh (74 μm).

In one embodiment of the present invention,
10 bentonite is used as binding agent. The amount of bentonite can be 0.5-1.0 w-%, preferably 0.6-0.8 w-%.

In one embodiment of the present invention,
fine carbon (coke) is added to the pelletizing feed. The amount of fine carbon can be 0.1-2.0 w-%, preferably
15 bly 0.5-1.0 w-%.

In one embodiment of the present invention, fluxing agent is added to the pelletizing feed. Suitable fluxing agents comprise, for instance, limestone, dolomite and quartzite.

20 In one embodiment of the present invention, the retention time in the drying zone is 6-8 minutes and temperature of the drying gas fed into the drying zone is 200-300° C, preferably 220-280° C. If the drying is carried out too violently, the pellets are broken
25 ken in the drying zone.

In another embodiment of the present invention, pellets are dried in two drying zones. In that case, the retention time in the first and second drying zone can be 7-8 minutes and 5-6 minutes, respectively,
30 tively, and the temperature of the drying gas fed into the first and second drying zone can be 150-250° C and 350-450° C, respectively.

In one embodiment of the present invention, the retention time in the heating zone is 5-12
35 minutes.

In one embodiment of the present invention, the retention time in the sintering zone is 7-14 minutes.

In one embodiment of the present invention, the material bed in the sintering zone is heated to a maximum temperature of 1200-1450° C, preferably 1250-1410° C, more preferably 1280-1390° C.

In one embodiment of the present invention, air from the cooling zone is re-circulated to at least one of the preceding zones.

Sintered manganese ore pellets manufactured by a process according to the present invention have a compressive strength of at least 150 kg/pellet of 12 mm diameter.

15

DETAILED DESCRIPTION OF THE INVENTION

The quality of manganese ore varies largely depending on the ore deposit. Manganese ores typically contain manganese oxides, silicates, carbonates, and hydrated components. The volatiles content of manganese ore fines can be up to 20.0%. Some manganese ores also contain calcites. Ore fines are generated, for instance, in excavation, crushing, screening and washing of manganese ore. This fines fraction can be used as a raw material in the production of sintered manganese ore pellets according to the present invention.

Manganese ore fines are preferably wet ground in a wet ball mill. The slurry from the wet grinding is filtrated to remove excess water. No further drying is needed. The filter cake forms the basis of pelletizing feed. The target fineness of the pelletizing feed is less than 50% under 400 mesh (38 µm) and 40-85%, preferably 55-70% under 200 mesh (74 µm).

Dry grinding of manganese ore fines is possible when the original ore contains only a little moisture.

If necessary, the ground manganese ore can be screened to produce finely divided manganese ore of the desired particle size.

Binding agent is added to the pelletizing
5 feed. The binding agent is preferably bentonite, which can be added to the pelletizing feed in an amount of 0.5-1.0 wt-%, preferably 0.6-0.8 wt-%. In the industrial scale production such amounts of bentonite are sufficient, whereas in the laboratory scale the
10 amounts of bentonite needed to produce acceptable pellets can be higher.

Depending on the composition of the finely divided manganese ore, fine carbon (coke or other carbon-bearing material) can optionally be added to the
15 pelletizing feed. The amount of fine carbon can be 0.1-2.0 w-%, preferably 0.5-1.0 w-%. Carbon addition is not needed when the manganese ore is in the oxidized form containing lots of MnO_2 . In that case a strong exothermic reaction between the carbon and oxygen tends to break the structure of the pellets. Carbon
20 can be used when the manganese ore contains a small amount of, for instance, carbonates as calcite. Small amounts of carbon can also be used when the manganese ore contains larger amounts of carbonates. Carbon
25 reactions liberate carbon monoxide (CO); this reaction is endothermic, limiting the increase of the bed temperature.

Depending on the composition of the finely divided manganese ore, fluxing agent can optionally be
30 added to the pelletizing feed. Suitable fluxing agents include limestone, dolomite, quartz, quartzite, wollastonite, and any mixtures thereof. Flux can be added when the bed temperature needs to be lowered. The need of flux depends of the mineralogy of the ore. Fluxes
35 are also needed when self-fluxing pellets are produced to minimize the need of flux addition in smelting.

The pelletizing feed consisting of finely divided manganese ore, bentonite, fine carbon and optional fluxing agent is mixed well. The moisture content of the pelletizing feed must be controlled very carefully. Pelletizing can be carried out in a rotary pelletizing drum or on a pelletizing disc. The discharge from the pelletizing device is preferably screened in a roller screen located under the discharge end of the pelletizing device. Usually, the oversize lumps are crushed and returned with the screen undersize as a recycling load back to the pelletizing feed production. Green pellets of a desired size can be dropped on a belt conveyor feeding to a shuttle feeder of a sintering furnace.

Sintering of green pellets can be carried out in a steel belt sintering furnace or a travelling grate sintering furnace. The pellet dust and dedusting of the sintering furnace are re-circulated back to the pelletizing feed.

A steel belt-type sintering furnace comprises an endless conveyor belt to transport the sintering feed through the stages of the sintering furnace. The thermal treatment in the sintering apparatus comprises the steps of drying, heating, sintering and cooling of the pellets.

The sintering furnace is preferably a multi-compartment oven through which the green pellets are carried on a perforated steel conveyor belt. A counter-current flow of cooling gases is arranged to carry waste heat from sintered pellets to those entering the front-end compartments. Typically, gases are sucked and cooling air blown through wind-boxes located under the conveyor belt. Preferably, sintered pellets are used as a bottom layer on the steel belt to protect it from too high temperatures.

The sintering furnace typically comprises at least one drying compartment as the first zone. In the

drying compartment, hot gas, which is preferably re-circulated from a third cooling zone, can be sucked through the bed and, as a consequence, the bed starts to dry. The temperature of the drying gas is preferably 200-400° C. The drying zone can be divided into two sections, especially when the moisture of the pellets is higher than 10%. Then the temperature in the first drying zone is in the range of 200-300° C. The drying temperature can be controlled by adjusting the cooling air flow through the third cooling zone. Typically, extra recycle gas is conducted to bypass the drying compartment.

The sintering furnace further comprises at least one heating compartment as the second zone. In the heating compartment, hot gas which is preferably re-circulated from a second cooling zone is sucked through the bed to increase the bed temperature. The bed is preferably heated to such a temperature where the carbon in the green pellet bed ignites to commence sintering reactions. The temperature of the heating gas is preferably 1050-1150° C. Preferably, the heat needed is obtained by burning fuel gas in a burner located in a circulating gas duct.

Further, the sintering furnace comprises a sintering compartment as the third zone to obtain sintered pellets. In the sintering compartment, hot gas, which is preferably circulated from a first cooling zone, is usually sucked through the bed. The temperature of the bed is preferably increased to the sintering temperature, which, depending on the mineralogy, can be 1200-1450° C. The maximum temperature of the sintering bed is preferably 1250-1410° C, more preferably 1280-1390° C. The heat necessary for the sintering stage can be obtained by burning fuel gas in a burner.

Preferably, process gases are separately taken out from each front-end zone to control the sin-

tering temperature, pressure and gas flow profiles in the sintering furnace. Typically, the gases are cleaned in wet scrubbers. The gas flows may be adjusted by controlling the speed of the off-gas fans.

5 In a preferred embodiment, the sintered pellets are cooled in one or more consecutive cooling compartments. The sintered pellets are cooled by blowing air through the bed from below the belt. The cooling gases may be circulated to the front-end compartments. Typically, air is blown separately to each
10 wind-box according to the pressure settings in the compartments over the bed. The sintering reactions usually still continue - at least partially - in the cooling zones to further strengthen the product pellets.
15

Typically, fresh sintered pellets are discharged together with bottom layer pellets and transported on the conveyor belt to screening and pellet bins. The final product pellets suitable for use as
20 smelting charge may be screened to a particle size of about 6-16 mm.

The compressive strength of sintered pellets is preferably over 150 kg/pellet of 12 mm diameter. The compressive strength represents the pellet's ability to resist compressive forces without breaking. It
25 is determined by placing pellets between two steel plates and evenly applying a measured pressure until the pellet fractures. Compressive strength is expressed as the applied pressure in kilogram per pellet. The compressive strength $F_{12\text{mm}}$ can be calculated
30 according to the following formula:

$$F_{12\text{mm}} = (12/D)^2 * F_D,$$

where

- D is the measured diameter of the pellet [mm];
- 35 - 12 is the reference diameter of the desired pellet [mm];

- FD is the measured compressive strength of the pellet [kg/pellet].

The total porosity of sintered pellets is preferably 10-50%, more preferably 12-40%. The true
5 density of the sintered pellets is preferably 3-5 g/cm³, more preferably 3.5-4.5 g/cm³.

The product received from the manganese pellet sintering furnace is a hard porous pellet with constant physical and chemical properties. The manga-
10 nese ore pellets produced according to the invention can be used as a starting material for the manufacture of ferromanganese, silicomanganese and ferrochromium manganese alloys.

The dust recycling load in the production of
15 sintered pellets is much lower than in the production of the conventional sintered product, as no crushing of sintered product is needed. The pellets endure handling and hauling without breakage or production of excessive amounts of dust.

20

EXAMPLE 1

Pelletizing and sintering tests were carried out in the laboratory scale with a sample of Brazilian manganese ore. The ore was of oxidized type and it
25 contained different types of hydroxides. The main phases of the sample comprised manganese oxides, pyrolusite, vernadite, todorokite, gibbsite, nacrite, kaolinite, silicon oxide, and mullite. The chemical analysis of the ore fines is shown in Table 1.

30 The pelletizing test was carried out on a laboratory disc with a diameter of 400 mm. The pelletizing mixture, consisting of dried manganese ore fines, bentonite, and calcite as a flux in some tests, was first mixed manually and then in a laboratory mixer.
35 The mixed batch was manually fed onto the pelletizing disc. The feed was moistened with a water sprayer in accordance with the formation of pellets. The desired

pellet diameter was 12 mm. After pelletizing the diameters and compressive strengths of the wet and dried pellets were measured. The moisture of the wet pellets was measured.

5

TABLE 1

Component	w-%
Mn	43.1
Fe	6.1
SiO ₂	4.5
CaO	0.27
MgO	0.36
Al ₂ O ₃	9.0
K	0.89
Na	< 0.04
S	0.12
C	0.17
Loss of ignition (LOI)	16.5
H ₂ O	8.2

The sintering tests were carried out in an induction furnace. The pellets were charged in a 110 ml alumina crucible. The crucible was placed into a large graphite crucible in the induction furnace. The graphite crucible was covered with a lid. Air was blown into the crucible throughout the test and the temperature was measured. The pellets were heated according to a desired temperature profile for steel belt sintering in the laboratory scale. The compressive strength target was 150 kg/pellet (proportioned to 12 mm size). The maximum temperatures in three tests were 1350° C, 1300° C and 1250° C. The retention time at the maximum temperature was 9-12 minutes.

When the pelletizing feed contained 100 units ore, 5.2 units calcite and 1.0 unit bentonite, the compressive strength of moist pellets was 1.5

kg/pellet and of dried pellets 7.8 kg/pellet. Compressive strengths of this order are high enough. The moisture content of the pellets was about 15%.

The compressive strength target of 200 kg/pellet of 12 mm diameter was achieved after sintering at 1300° C. The compressive strengths after sintering steps carried out at different maximum temperatures are shown in Table 2.

10 **TABLE 2**

Maximum temperature	Compressive strength
1250° C	121 kg/pellet
1300° C	231 kg/pellet
1350° C	300 kg/pellet

The test results indicate that good quality sintered pellets can be produced in an industrial scale process.

15

EXAMPLE 2

Batch sintering tests were carried out in the pilot scale with two South African manganese ores Z1 and Z2 and a Brazilian manganese ore Z3.

20

Test procedures

The test samples were ground to produce the desired fineness of manganese ore fines for the batch pelletizing and sintering tests. Grinding was carried out with a pressure grinding mill and a vibrating Pal-
25 la mill at a dry state.

The purpose of batch pelletizing was to study the pelletizing properties of finely divided manganese ore and also to produce pellets for batch sintering tests. The ground manganese ore fines were mixed with bentonite. In some cases also coke was added. Pelletizing tests were performed using a pelletizing disc. The batch was fed manually onto the disc. The
30

pelletizing feed was moisturized with water sprayer according to the formation of pellets. The desired grain size of pellets was 12 mm.

Sintering tests were performed using a batch
5 sintering system, which consists of a butane burner, combustion chamber, sintering reactor, and the necessary gas lines. The gas lines were equipped with the necessary water-cooled valves to lead combustion gases to the reactor and off-gases to a gas cleaning system.
10 The sintering process was controlled continuously by an automatic process control system.

The batch sintering process comprised the following zones:

- 1) drying with combustion gases;
- 15 2) heating with combustion gases using oxygen enrichment;
- 3) sintering with combustion gases using oxygen enrichment; and
- 4) cooling with air or nitrogen.

20 In some tests the drying and heating zone was divided into two different zones. The amount of gas feed and retention time were pre-selected for each zone. The temperature of the combustion gases was controlled by the amount of butane, air ratio, and oxygen
25 enrichment. The combustion gases entered the reactor from above. Also the cooling gas was ducted into the reactor from above. In the industrial scale processes the combustion gases and cooling gases would be fed to the material bed from beneath.

30 Moist green pellets were charged into the reactor on a bottom layer consisting of previously sintered brown pellets. The height of both layers was about 200 mm. After the sintering program was completed, the batch reactor was cooled to below 100° C and
35 the sintered pellets were discharged from the reactor. The bed of sintered pellets was divided into three different sections for the laboratory tests. The sec-

tions were an upper section (50 mm), a middle section (100 mm), and a lower section (50 mm). The protective bottom layer was changed after every test.

5 Test materials

The manganese ore fines used as test material were originally too coarse for pelletizing, which is why they had to be ground. The test materials were ground in dry state. The target fineness was less than 50% under 400 mesh (38 μm) and 65-70% under 200 mesh (74 μm). These target values are coarser than those usually used in chromite pelletizing and sintering in order to avoid breakage of pellets due to decomposition of volatile components of the ore.

The grain size of the ground manganese ore fines Z1-Z3 used in the batch pelletizing and sintering tests is shown in Table 3. Z1 and Z2 represent the manganese ore fines from South African deposits and Z3 represents the manganese ore fines from a Brazilian deposit.

TABLE 3

Screen size		Z1	Z2	Z3
mesh	mm	undersize, %		
30	0.600	100.0	99.3	
70	0.212	98.5	95.4	
200	0.074	66.9	64.7	55.8
400	0.038	46.8	46.9	45.5

The chemical analyses of the tested manganese ore materials Z1-Z3 are shown in Table 4.

Z1 manganese ore contained much more volatiles than Z2 manganese ore due to its high content of calcite. The high calcium content of Z1 manganese ore needs to be taken into account in smelting.

Z2 manganese ore was richer in manganese than Z1 manganese ore, but its Mn/Fe ratio was clearly low-

er than that of Z1 manganese ore. In Z2 manganese ore water was combined with different hydroxides.

Z3 manganese ore had also quite high volatile content. Z3 manganese ore was oxidized ore and it contained also a plenty of hydroxides.

TABLE 4

Component	Z1 (w-%)	Z2 (w-%)	Z3 (w-%)
Mn	36.9	48.9	41.1
Fe _{tot}	4.9	11.1	6.9
Fe ²⁺	0.0	0.0	-
Fe ³⁺	4.9	11.1	6.9
SiO ₂	6.1	6.2	6.2
Al ₂ O ₃	0.22	0.3	8.8
MgO	3.7	0.5	0.2
CaO	12.8	4.7	0.3
BaO	0.22	0.6	-
Na ₂ O	0.02	0.02	0.1
K ₂ O	0.01	0.01	1.1
CO ₂	13.6	1.0	-
H ₂ O	3.7	2.7	6.9
Volatiles	(17.3)	(3.7)	(15.4)
Mn/Fe	7.53	4.40	5.96

As regards the main phases of the test materials, Z1 manganese ore fines could be divided into three mineralogical types: manganese oxides, silicates and carbonates. The manganese phases in the carbonate-based particles were disseminated. The manganese oxide phase appeared as bixbyite (Mn₂O₃) and hausmannite (Mn₃O₄) grains. The silicate phase consisted of manganese silicate grains, such as braunite and caryoplite. The carbonate phase appeared as kutnorite and calcite grains.

The microstructure of Z2 manganese ore fines was different from that of Z1 manganese ore fines. The

Z2 manganese ore did not contain as much carbonate as Z1 manganese ore. Z2 manganese ore could be divided into two morphological types: manganese oxides and silicates. The manganese oxides appeared as bixbyite and hausmannite. The silicate phase consisted of braunite, calcium manganese silicate and bementite. These oxide and silicate phases were very finely disseminated. The silicate grains also contained inclusions of iron oxides. The carbonate appeared as calcite.

Z3 manganese ore fines were of oxidized type. The manganese ore contained mainly three hydrated components: vernandite, gibbsite and goethite. The hydroxides contained impurities. The manganese hydroxide contained a small amount of iron and aluminum. Manganese and aluminum also formed hydrosilicate. Iron appeared as goethite which contains aluminum. Z3 manganese ore also contained pure MnO_2 and SiO_2 grains. Potassium and barium appeared in manganese hydroxides.

Test results

The target of the pelletizing and sintering tests was to find proper sintering conditions to produce suitable pellet grade for smelting in an electric furnace. The studied parameters were the retention time and temperature in different sintering zones and coke addition. The same amount of bentonite was used in every test.

Altogether 23 pelletizing and batch-sintering tests were carried out. Z2 manganese ore was used in 8 tests and Z1 manganese ore in 11 tests. Two tests were carried out with the mixture of Z1 and Z2. Z3 manganese ore was used in two tests. In the following the results of each ore are presented and commented separately. Many results of Z3 ore are taken from some earlier studies made with the same ore and compared to the results of these investigations.

Strength of Z2 pellets

The compressive strength of the sintered pellets of Z2 manganese ore was very high. Water addition was controlled very carefully during the pelletizing of the ore. Pellets became sticky and they also lost their round shape, easily becoming elliptical due to excess moisture. Coke addition made pelletizing more difficult.

The moisture content of the green pellets was in the range of 6.1-7.5%. The wet strength was 2.2-2.7 kg/pellet and the dry strength was 4.6-6.4 kg/pellet. These strength values are high enough.

The compressive strength of the sintered pellets was very high in some tests. Compressive strengths of over 300 kg/pellet could be measured. The pellet size shrank a little during the sintering.

In a test resulting in the production of acceptable pellets, the maximum temperature of the drying gas was 300° C. The feed gas temperature was increased to 1150° C when cooling was started. The maximum temperature in the bed was about 1200° C at the bottom, 1250° C in the middle, and 1280° C on the top of the bed. The total retention time in the drying, heating and sintering zones was 22.5 minutes.

The compressive strength of the sintered pellets of Z2 manganese ore was good in many process conditions. The minimum total retention time, without cooling, was 21.5 minutes. The drying time varied between 6 and 8 minutes. The heating time was 5-12 minutes and the sintering time was 7-14 minutes.

The strength values were satisfactory when no coke was used or the carbon addition was 1% C_{fix}.

Strength of Z1 pellets

Pelletizing of Z1 manganese ore was easy and coke addition made it even easier. The compressive

strength of the pellets made from Z1 manganese ore fines was at first clearly lower compared to the pellets of Z2 manganese ore. The parameters needed to produce good pellets for smelting were determined.

5 The moisture content of green pellets was 6.8-7.2%. The wet strength was 2.6-3.4 kg/pellet and the dry strength was 11.8-16.2 kg/pellet. These strength values are high enough. The dry strength of Z1 manganese ore pellets was about two times higher
10 than the dry strength of Z2 manganese ore pellets.

The pellets shrank considerably in the sintering. This is probably due to the high amount of calcite, which decomposes during sintering.

15 The batch sintering tests show that the pellets of Z1 manganese ore start to melt around 1400° C, which therefore forms an upper temperature limit in sintering.

20 The compressive strength of sintered pellets was acceptable (over 200kg/pellet, not proportioned to 12 mm) in some of the tests. The best results were achieved when the total retention time in drying, heating and sintering steps was 24-26 minutes.

25 Carbon addition of 0.5% C_{fix} seemed to be high enough to keep the temperature in the bottom layer of the material bed high enough. Larger coke amounts seemed to make the pellets even weaker. Coke creates a reducing atmosphere inside the pellets, which may reduce the manganese oxides and consume energy. Decomposition of calcite liberates CO₂ which reacts with the
30 carbon inside the pellets. This consumes energy and the gas volume increases. These factors may degrade the compression strength of the pellets.

35 As an example, in one successful sintering test the temperature of the drying gas was about 300° C at the end of the drying period. The maximum temperature in the bed was a little below 1400° C. The temperature of the feed gas was 1200° C before cooling

was started. The temperature in the middle of the bed was 1300-1350° C.

Strength of Z3 pellets

5 The particle size distribution of Z3 manganese ore was almost the same as that of Z2 and Z1 manganese ores. The pelletizing succeeded well. Both the wet and dry strengths of the green pellets were high enough.

10 The pellets shrank considerably during the sintering. The compressive strength of the Z3 sintered pellets was not very good if the total retention time in the sintering process was too short.

 In the investigations performed with Z3 manganese ore, a compressive strength of about 300 kg/pellet of 10 mm diameter was yielded, which is very good. In the tests the total retention time in the sintering process (drying, heating and sintering, without cooling) was 29 minutes, which was long enough. The retention times in the two stages of drying were 7-8 minutes and 5-6 minutes. Thus the total drying time was 12-14 minutes.

Other properties of sintered pellets

25 The abrasion resistance of sintered pellets was studied using a modified Tumbler method. The batch consisted of a sample of 1 kg. The test was performed in a steel drum equipped with six lifters. After 90 minutes rotation time the entire batch was screened with 0.6 mm and 5.0 mm sieves. The abrasion resistance value indicates the durability of the pellets against abrasion. The lower the value, the higher is the abrasion resistance of the pellets. Abrasion resistance values for sintered pellets are shown in Table 5.

35 The modified Tumbler values of Z1 and Z3 pellets were excellent. The abrasion resistance of Z2 pellets was the highest although their compressive

strength was excellent. However, the Tumbler value of Z2 pellets was at the same level as that of chromite ore pellets.

5 **TABLE 5**

Ore	< 5 mm	< 0.6 mm
Z2	7.3	7.3
Z1	0.5	0.5
Z3	1.0	1.0

Density and porosity are often used to describe the structure of the sintered pellets. The density and porosity of sintered pellets taken from the middle layer of the material bed are shown in Table 6.

True density is the mass divided by the volume of the pellet, the volume not including the pore spaces within the pellet. True density was measured using a He-pycnometer. For this determination, the pellets were ground to a grain size of -74 μm .

TABLE 6

Ore	Density, g/cm ³		Porosity, %	
	true	bulk	total	apparent
Z2	4.49	3.76	26.4	14.3
Z1	4.24	3.55	39.4	10.0
Z3	4.06	3.59	14.0	8.3

Bulk density is the mass divided by the volume of the pellet, the volume also including the inter-granular spaces, i.e. the porosity factor. The diameter of twenty pellets was measured, each from three directions, and the mean diameter was calculated. The pellets were weighed together. The mean weight of the pellets and the bulk density were calculated.

Total porosity was calculated based on the bulk density and the true density.

Apparent density was determined in deionised water under vacuum. Twenty pellets were weighed and put into a beaker and weighed together. The beaker was filled with deionised water to an exact volume. The beaker with pellets and water was weighed. The pellets with water were decanted into a suction bottle containing water. The bottle was connected to a vacuum pump. Air was removed from the pellets under vacuum. The pellets were weighed with the open porosity full of water. Apparent density was calculated based on the mass of dry pellets, bulk volume of dry pellets, mass of water in the open porosity and the density of water.

The total porosity of Z1 pellets was very high and much higher than the total porosity of Z2 pellets. The main reason for the difference in porosity can be the fact that the Z1 manganese ore contained much more volatiles than the Z2 manganese ore.

The pellets of Z3 manganese ore had the lowest porosity. Those pellets shrank considerably in the sintering. Furthermore, there seemed to be melt phases on the surface of Z3 pellets.

The true and bulk densities of Z2 pellets were higher than the densities of the other pellets.

Pellets from selected sintering tests were chemically analyzed. The results of these chemical analyses are presented in Table 7.

TABLE 7

Ore	Mn	Fe _{tot}	SiO ₂	Al ₂ O ₃	CaO	MgO	K ₂ O	S	LOI	Mn/Fe
Z2	49.3	10.5	7.1	0.53	4.8	0.64	<0.02	0.11	-	4.7
Z1	44.0	5.8	9.0	0.47	14.5	4.2	<0.02	0.02	-	7.6
Z3	47.0	8.4	8.5	10.4	0.35	0.28	1.2	0.11	0.78	5.6

The manganese content of Z3 and Z1 pellets was much higher than that of the original ores. This is due to the big weight loss of the ore in sintering, especially the decomposition of volatiles. The aluminum content of Z3 pellets was much higher than that of Z1 and Z2 pellets. The calcium content of the Z1 pellets was high. This will make it possible to use the "discard slag method" in smelting.

These pilot scale tests gave information about optimal conditions to be used in pelletizing and sintering of manganese ore fines. Ground manganese ore fines are suitable for pelletizing. The compressive strength of wet and dry pellets is high enough. Manganese pellets disintegrate very easily during the drying, which is why the drying should be performed very carefully. Sintering conditions should be selected based on the composition of the manganese ore fines.

CLAIMS

1. A method for producing sintered manganese ore pellets, comprising the steps of:

5 - producing a pelletizing feed comprising finely divided manganese ore and binding agent;

 - pelletizing the pelletizing feed to produce green pellets; and

10 - sintering the green pellets in a steel belt sintering furnace, the sintering step comprising conveying the pellets on a steel belt through process zones of different temperatures, the process zones including at least one drying zone, at least one heating zone, at least one sintering zone, and at least one cooling zone, preferably three.

15 2. A method according to claim 1, comprising the step of producing finely divided manganese ore from manganese ore fines by wet grinding and filtering.

20 3. A method according to claim 1, comprising the step of producing finely divided manganese ore from manganese ore fines by dry grinding.

25 4. A method according to claim 2 or 3, comprising grinding and screening the manganese ore to produce a particle size distribution comprising less than 50% below 400 mesh (38 μm) and 40-85%, more preferably 55-70% below 200 mesh (74 μm).

 5. A method according to any one of claims 1 to 4, wherein bentonite is used as binding agent, the amount of bentonite being 0.5-1.0 w-%, preferably 0.6-0.8 w-%.

30 6. A method according to any one of claims 1 to 5, comprising adding fine carbon to the pelletizing feed, the amount of fine carbon being 0.1-2.0 w-%, preferably 0.5-1.0 w-%.

35 7. A method according to any one of claims 1 to 6, comprising adding fluxing agent to the pelletizing feed.

8. A method according to any one of claims 1 to 7, wherein the retention time in the drying zone is 6-8 minutes and temperature of the drying gas fed into the drying zone is 200-300° C, preferably 220-280° C.

5 9. A method according to any one of claims 1 to 7, comprising drying the pellets in two drying zones, the retention time in the first and second drying zone being 7-8 minutes and 5-6 minutes, respectively, and the temperature of the drying gas fed into
10 the first and second drying zone being 150-250° C and 350-450° C, respectively.

10. A method according to any one of claims 1 to 9, wherein the retention time in the heating zone is 5-12 minutes.

15 11. A method according to any one of claims 1 to 10, wherein the retention time in the sintering zone is 7-14 minutes.

12. A method according to any one of claims 1 to 11, wherein the material bed in the sintering zone
20 is heated to a maximum temperature of 1200-1450° C, preferably 1250-1410° C, more preferably 1280-1390° C.

13. A method according to any one of claims 1 to 12, wherein the total retention time in the drying, heating and sintering zones is 20-35 minutes, preferably
25 bly 21-30 minutes, more preferably 22-26 minutes.

14. A method according to any one of claims 1 to 13, wherein air from the cooling zone is recirculated to at least one of the preceding zones.

15. Sintered manganese ore pellets manufactured by a process according to any one of claims 1 to
30 14, wherein the compressive strength of the sintered pellets is at least 150 kg/pellet of 12 mm diameter.

INTERNATIONAL SEARCH REPORT

International application No
PCT/FI2014/051010

A. CLASSIFICATION OF SUBJECT MATTER

INV. C22B1/20 C22B1/243 C22B1/245 C22B1/24
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C22B

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

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

EPO-Internal, COMPENDEX, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	US 6 063 160 A (KROGERUS HELGE [FI] ET AL) 16 May 2000 (2000-05-16) cited in the application the whole document	1-15
X	CN 103 014 326 A (CHANGSHA RES INST MINING & METALLURG CO LTD) 3 April 2013 (2013-04-03) the whole document	1-15
X	WO 2010/009527 A1 (VALE SA [BR]; MAFRA WASHINGTON LUIZ [BR]; SOUZA JOAO BATISTA CONTI DE) 28 January 2010 (2010-01-28) cited in the application the whole document	1-15

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Further documents are listed in the continuation of Box C.

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See patent family annex.

* Special categories of cited documents :

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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