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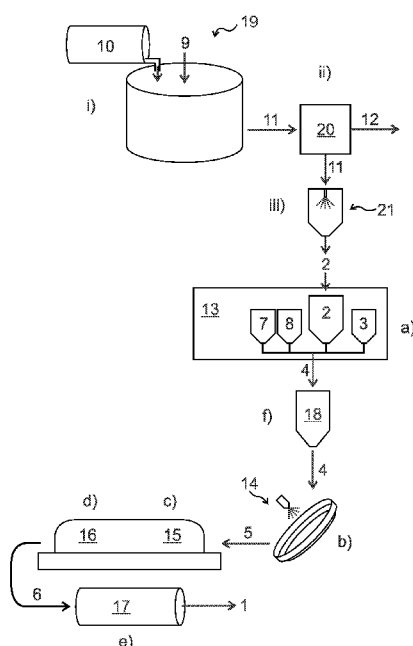
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PLANT FOR THEIR PRODUCTION

FIG. 4



(57) Abstract: The disclosure relates to a method for producing reduced manganese (Mn) pellets (1). The method is characterized in that the method comprises the steps of a) mixing dried manganese sulfate (MnSO₄) fraction (2) with binder (3) to form a pelletizing mixture (4); b) pelletizing the pelletizing mixture (4) to produce Mn pellets (5); c) drying the Mn pellets (5); d) sintering the dried Mn pellets (5) to produce sintered pellets (6); and e) reducing the sintered pellets (6) for obtaining reduced Mn pellets (1). The disclosure further relates to ferromanganese pellets obtainable by the method according to the present disclosure and to a plant for producing reduced Mn pellets.

METHOD FOR PRODUCING REDUCED MANGANESE PELLETS, REDUCED MANGANESE PELLETS AND A PLANT FOR THEIR PRODUCTION

5 **TECHNICAL FIELD**

The current disclosure relates to a method for producing reduced manganese pellets, to reduced manganese pellets and a plant for their production.

10 **BACKGROUND**

Ferromanganese is used in steelmaking to provide the manganese utilized as an alloying element or as a deoxidizing agent. Ferromanganese is produced from iron- and manganese-containing ores by smelting
15 oxides of manganese and iron in the presence of reductants and fluxing agents in a furnace. This process results in reduced ferromanganese.

However, the process requires the ore to have sufficiently high manganese content. The ratio of manganese to iron should be approximately 8 for the production of standard ferromanganese or high-carbon ferromanganese (HCF_{FeMn}). Therefore, low-grade manganese
20 ores, having a lower Mn/Fe ratio are supplemented with higher-grade manganese ore, or with manganese sinter to allow their utilization in the production of ferromanganese.
25

Drawbacks of the prior art methods include the need to transport the high-grade manganese ore, possibly long distances. The reduction of manganese
30 oxides and iron oxides in the furnace is energy-intensive and increases the electricity consumption during the process. The inventors have therefore recognized the need for a method for producing ferromanganese from low-grade ores.

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SUMMARY

The purpose of the current disclosure is to provide a new type of method for producing reduced manganese (Mn) pellets that can be used in ferromanganese production. The purpose of the current disclosure is also to provide a plant for producing reduced Mn pellets. Also the purpose is to provide new type of reduced Mn pellets and their use. Further, the purpose is to alleviate at least one of the disadvantages mentioned above.

The method according to the current disclosure is characterized by what is presented in claim 1.

The reduced manganese pellets according to the present disclosure are characterized by what is presented in claim 15.

The use of the reduced manganese pellets according to the present disclosure is characterized by what is presented in claim 17.

The plant according to the current disclosure is characterized by what is presented in claim 18.

The method and the plant according to the present disclosure can offer at least one of the following advantages over prior art:

Low-grade manganese ores can be utilized in the production of ferromanganese. This may reduce the need to transport manganese ore for processing, thus reducing cost and environmental impact of ferromanganese production.

The manganese is at least partially reduced during the method steps. This may reduce the electricity consumption during smelting. It is also possible to obtain ferromanganese with high metallization degree with lower electricity consumption, or to increase metallization degree while keeping electricity consumption moderate.

BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying drawings, which are included to provide a further understanding of the current disclosure and constitute a part of this specification, illustrate embodiments of the disclosure and together with the description help to explain the principles of the current disclosure. In the drawings:

Fig. 1 is a flow chart illustration of an exemplary embodiment of the method according to the present disclosure.

Fig. 2 is a flow chart illustration of another exemplary embodiment of the method according to the present disclosure.

Fig. 3 is a flow chart illustration of yet another exemplary embodiment of the method according to the present disclosure.

Fig. 4 is a schematic presentation of an exemplary embodiment of a plant according to the present disclosure.

Fig. 5 is a schematic presentation of another exemplary embodiment of a plant according to the present disclosure.

Fig. 6 is a schematic presentation of yet another exemplary embodiment of a plant according to the present disclosure.

DETAILED DESCRIPTION

In one aspect, a method for producing reduced manganese (Mn) pellets is disclosed. The method comprises the steps of

- a) mixing dried manganese sulfate (MnSO_4) fraction with binder to form a pelletizing mixture;
- b) pelletizing the pelletizing mixture to produce Mn pellets;
- c) drying the Mn pellets;

d) sintering the dried Mn pellets to produce sintered pellets; and

e) reducing the sintered pellets to obtain reduced Mn pellets.

5 In the method according to the present disclosure, dried MnSO_4 fraction is used as starting material for producing reduced Mn pellets. The MnSO_4 fraction may be obtained by leaching from MnCO_3 -containing ore.

10 The reduced Mn pellets may be used in smelting with manganese ore or with manganese ore sinter in order to produce ferromanganese. The end product after smelting may be standard HCFMn (high-carbon ferromanganese). The Mn content of ferromanganese can be increased by using the Mn pellets obtainable by the
15 method according to the present disclosure. The starting material for the current method, i.e. dried MnSO_4 fraction may be obtained from the same ore that is being smelted to produce ferromanganese. This might allow the utilization of local lower-grade manganese
20 ores without the need to bring in ores of higher manganese content or manganese sinter from other locations. Further, the reduced Mn pellets obtainable by the current method may be transported and used elsewhere. Thus, the reduced Mn pellets according to the
25 present disclosure might have commercial value on their own. This might allow the utilization of manganese carbonate ore deposits, which have thus far been abandoned as uneconomical.

30 By dried MnSO_4 fraction is herein meant solid material comprising mainly of MnSO_4 , typically present as various hydrates. The dried MnSO_4 fraction might also contain small amounts of iron, aluminum, magnesium, as well as other elements. The manganese-to-iron
35 (Mn/Fe) ratio of the dried MnSO_4 fraction is above 8, for example, 11-14. In one embodiment, the manganese-to-iron ratio of the dried MnSO_4 fraction is at least

10, or at least 12. The dried MnSO_4 fraction may have variable water content depending on the process specifics. It can contain, for example, 10-30 w-% water. The dried MnSO_4 fraction may contain approximately 20-
5 25 w-% water.

A loss-on-ignition (L.O.I.) value describes the proportion of volatile substances degraded upon heating to, for example 900 °C or 1,000 °C under neutral atmosphere, such as N_2 or Ar. For the dried MnSO_4
10 fraction, L.O.I. can be over 50%. L.O.I. may be, for example, 60% or 63%. For the purposes of the current disclosure, L.O.I. is measured according to methods known in the art.

15 The preparation of the dried MnSO_4 fraction influences its grain size, which, in turn, has an effect on its behavior during further processing. Typically, grain size of below 150 μm is suitable for the current method. The grain size of the dried MnSO_4
20 fraction may be, for example, 20-120 μm . While the majority of the particles can have a grain size of approximately 30-80 μm , the size distribution of the particles might vary. If the dried MnSO_4 fraction is crushed before use, the particle size distribution is
25 different than when the MnSO_4 fraction is dried by spray-drying. Generally finer material is more amenable for pelletization, but more prone to dust formation during processing.

In step a) of the process, the dried MnSO_4
30 fraction is mixed with binder to form a pelletizing mixture. The binder is typically bentonite. The use of bentonite as a binder is known to the skilled person. 0.8 - 2 w-% bentonite compared to the weight of the ore raw material may be used. Alternatively, 0.8 - 2
35 w-% bentonite compared to the weight of the ore supplemented with fluxing agent may be used.

In one embodiment, carbonaceous material and/or fluxing agent is mixed with the dried MnSO_4 fraction at step a). In addition to the binder, carbonaceous material may be mixed with the dried MnSO_4 fraction and the binder. In addition to the binder, fluxing agent may be mixed with the dried MnSO_4 fraction and the binder. Either fluxing agent or carbonaceous material or both may be mixed with the dried MnSO_4 fraction and the binder. Examples of carbonaceous materials include coke, anthracite and charcoal. Examples of fluxing agents include quartz, wollastonite, calcite and dolomite. The different components to be mixed in step a) can be added sequentially in any order, simultaneously or gradually.

At step b), the pelletizing mixture is pelletized. Water may be added to the mixture while it is being agitated in a disc pelletizer until suitable pellets are formed. The moisture content of the resulting pellets is between 10 and 25 w-%. For example, the moisture content may be 12-14 %.

At step c), the Mn pellets obtained in step b) are dried with methods known in the art. The drying may be performed in a dedicated device, or in the same device in which the sintering of step d) is performed.

At step d), the dried Mn pellets are sintered. At this step, any MnSO_4 that might still be present in the pellets might degrade practically completely. Typically, the sintered pellets have a diameter of 10-14 mm, for example 12 mm. The compressive strength of the sintered pellets is 60-220 kg/pellet, or 140-220 kg/pellet for a pellet of 12 mm diameter. The compressive strength may be, for example 170, 200 or 210 kg/pellet for a pellet of 12 mm diameter. The compressive strength of the sintered pellets is sufficient for industrial-scale reduction at step e).

In one embodiment, the sintering in step d) is performed by travelling-grate sintering or steel belt sintering.

In one embodiment, the sintering in step d) is performed at a temperature of at least 1,200 °C for at least 10 minutes. The sintering at step d) may be performed at a temperature of 1,350 - 1,550 °C. As an example, a temperature of 1,400 °C or 1,500 °C may be used. The length of sintering at step d) may be, for example, 10-20 minutes. In an embodiment, the length of sintering at step d) is 15 minutes. It should be noted that the heating and cooling during sintering do not happen instantaneously. Therefore, the temperatures and times given above should not be taken as absolute values, as is known to the skilled person.

At step e) of the method, the sintered pellets are reduced. Reduced Mn pellets are produced. In one embodiment, the reduction in step e) is performed at a temperature of at least 1,200 °C, or at a temperature of 1,300 °C, or at a temperature of 1,350 °C. The reduction is performed in the presence of carbonaceous reductants.

Due to the previous process steps, the level of impurities in the sintered pellets might be low enough to allow the use of high reduction temperatures without adverse effects on the reduction. The reduction time may vary between 30 minutes and 3 hours. For example, the reduction at step e) may be performed for 1 hour. The temperature and time used at step e) depend, among other things, on the targeted metallization degree of the reduced Mn pellets. Also the composition of the carbonaceous reductant may affect the metallization degree of the reduced Mn pellets. Examples of available carbonaceous reductants are coke, anthracite and charcoal.

Typically, to reach a given metallization degree, shorter reduction time is sufficient if higher temperatures are used, and vice versa. A high metallization degree can offer advantages during subsequent
5 smelting of ferromanganese, as the electricity consumption in the smelting furnace may be reduced.

In one embodiment, the reduction in step e) is performed in a rotary kiln or in a direct reduction furnace. In an embodiment, the reduction in step e) is
10 performed in a rotary kiln. For example natural gas or heavy fuel oil may be used to fuel the rotary kiln. In an embodiment, the reduction in step e) is performed in a direct reduction furnace. An example of a direct reduction furnace is a Midrex furnace. Remaining carbonaceous reductant may be removed from the reduced Mn
15 pellets, if needed. For example magnetic methods can be used. The necessity of carbonaceous reductant removal depends on the further processing steps and may be assessed by the skilled person.

20

In one embodiment, the method further comprises step f) of calcinating the dried MnSO_4 fraction before step a), or the pelletizing mixture after step a), or the Mn pellets after step c). Since calcination
25 removes volatiles from the dried MnSO_4 fraction, also a part of the sulphur is removed from the dried MnSO_4 fraction. Also crystalline water present in the dried MnSO_4 fraction is removed during calcination. Calcination may have the advantage that it improves the compressive strength of the sintered pellets. Calcination
30 at step f), may be performed in a fluidized bed furnace. Other types of means for calcination are known. In one embodiment, the calcination in step f) is performed in a fluidized bed furnace. Alternatively, the calcination at step f) may be performed in a chamber
35 furnace. A rotary kiln or a shaft furnace may also be used. Further alternative is a multiple hearth fur-

nace. The calcination may be performed at a temperature between 400-1,100 °C. In an embodiment, the calcination in step f) is performed at a temperature of 800 °C. In an embodiment, the calcination in step f) is performed at a temperature of 1,000 °C. The duration of calcination may vary. The calcination in step f) may be performed for 1-5 hours. For example, the calcination time may be 2 or 3 hours. Sufficient calcination time depends on the calcination temperature and grain size of the material, as well as on the targeted degree of volatile substance removal.

In one embodiment, steps c), f) and d) are performed in one device, such as a sintering furnace comprising a plurality of process zones. The steps are performed in the order indicated, i.e. first step c), then step f), then step d). Examples of sintering furnaces are travelling-grate sintering furnace or a steel belt sintering furnace. The temperature conditions in each process zone may be independently controllable. Each process zone may comprise one or more burners for controlling the temperature in the respective process zone. The process zones comprise at least one drying zone, at least one heating zone, at least one sintering zone and at least one cooling zone. The drying of step c) may be performed in one or more drying zones. The calcination of step f) may be performed in one or more of the heating zones. The sintering of step d) may be performed in one or more sintering zones.

For example, there may be two drying zones in which step c) is performed (i.e. process zones I and II). The retention time in each process zone for step c) may be 4-8 minutes, for example 6 minutes. In the first process zone (I), gas temperature may be 250 - 350 °C. In the second process zone (II), gas temperature may be 350 - 500 °C.

Process zones I and II may be followed by two heating zones for performing step f) (i.e. process zones III and IV). The retention time in each process zone for step f) may be 4-8 minutes, for example 6
5 minutes. In the third process zone (III), gas temperature may be 400-1,000 °C. In the fourth process zone (IV), gas temperature may be 600-1,250 °C. In an embodiment, gas temperature in process zone III is 900 °C. In an embodiment, gas temperature in process zone
10 IV is 1,100 °C.

Process zones III and IV may be followed by a sintering zone for performing step d) (i.e. process zone V). The retention time in the process zone for step d) may be 4-8 minutes, for example 5 or 6
15 minutes. In the fifth process zone (V), gas temperature may be 1,000-1,350 °C. The bed temperature during step d) may exceed the gas temperature due to exothermic processes in the pellets. Carbonaceous material, such as coke, may be added to adjust the bed temperature. The amount of carbonaceous material may be 1-2
20 w-% compared to the weight of the pellets.

By bed temperature is herein meant the temperature inside the material to be treated, which may differ from the gas temperature, i.e. from the temperature of the gas surrounding the material. Typically,
25 the bed temperature might be higher than gas temperature. For example, the bed temperature during sintering (step d) may be 1,400 °C or higher. The bed temperature during step d may be 1,450 °C, or 1,500 °C.

30 Process zone V may be followed by one or more cooling zones (process zone VI, and optionally VII etc.) for lowering the temperature of the sintered pellets in a controlled manner.

Each process zone I-VI(VII) may comprise a
35 burner for regulating gas temperature in that process zone. For example, CO gas from an electric furnace may

be used for fueling the burners. Also natural gas or LPG gas may be used.

The pellets proceed through the process zones in the described order, resulting in the production of
5 sintered pellets.

The process steps a), b), c), d), e) and f) according to the present disclosure may follow each other directly. Alternatively, the material may be
10 stored between steps. Intermediate storage might be advantageous in regulating the amount of material directed to each process step.

In one embodiment, the method further comprises the steps of

15 i) leaching manganese (Mn)-containing MnCO_3 ore with sulphuric acid for producing manganese sulfate (MnSO_4) leachate;

ii) separating MnSO_4 leachate from residual ore; and

20 iii) drying the MnSO_4 leachate for producing dried MnSO_4 fraction.

The method according to the present disclosure may comprise leaching, separation and drying steps i)-iii) to obtain the dried MnSO_4 fraction used
25 for step a) or f). Depending on the embodiment, step iii) is followed by step a) or by step f). Alternatively, dried MnSO_4 fraction obtained by other means can be used. If the method comprises steps i) to iii), they do not need to be performed directly before the
30 further process steps. It is possible to store and/or to transport the dried MnSO_4 fraction, or the intermediate products, before further processing. The manganese-containing ore used at step i) may be Mn-carbonate ore comprising MnCO_3 ($\text{MnO} \cdot \text{CO}_2$).

35 At step i) Mn-containing ore is exposed to sulphuric acid (H_2SO_4). The Mn-containing ore may be crushed before step i). Sulphuric acid of variable

grades and/or strengths can be used for leaching. The leaching may be brought about by different leaching techniques known in the art, such as tank leaching, dump leaching, heap leaching and in-situ leaching.

5 When appropriate, heating and/or mixing may be used to enhance the leaching process. The skilled person is able to take account the properties of sulphuric acid to accomplish a safe leaching procedure.

At step ii) the MnSO_4 leachate is separated
10 form residual ore. The separation at step ii) may comprise one or more stages. Different separation techniques may be applied. Depending on the targeted purity of the MnSO_4 and the desired speed of processing, suitable process steps and parameters can be selected.

15 When MnSO_4 is dissolved, undissolved material may be removed by separating the solid and liquid phases. For example, MnSO_4 can be separated as a filtrate, whereas the residual ore remains in the filter as a solid phase. Sedimentation-based methods may be used. An example of such is centrifugation. Alternatively or in
20 addition, MnSO_4 may be specifically precipitated, leaving impurities in liquid phase.

Depending on the method of leaching, step ii) may be performed in batch or continuously. In one embodiment, the separating in step ii) comprises filtration. In an embodiment, the separating at step ii) comprises sedimentation or centrifugation.

At step iii), the MnSO_4 leachate is dried. In one embodiment, the drying in step iii) comprises
30 spray drying. Spray drying might be beneficial, as the particle size might allow the direct further treatment by mixing at step a) or calcination at step f) without intermediate processing steps. The method may comprise a further step iv) of crushing and optionally grinding
35 the dried MnSO_4 fraction after step iii).

The process steps i), ii) and iii) according to the present disclosure may follow each other di-

rectly. Alternatively, the material may be stored between steps. Intermediate storage might be advantageous in regulating the amount of material directed to each process step.

5

In one embodiment, the manganese-containing ore comprises 30-40 w-% of elemental manganese and 5-15 w-% elemental iron (Fe). The starting material for the current method may be practically any Mn-containing MnCO₃ ore. However, the utilization of the current method might be especially advantageous for low-grade Mn ores, in which the Mn/Fe ratio is below 8. For example, the Mn/Fe ratio might be 6 or 4. It might be possible to utilize Mn-containing ores with a Mn/Fe ratio of approximately 2.5.

In one aspect, reduced Mn pellets obtainable by the method according to present disclosure are disclosed. The reduced Mn pellets are characterized in that the metallization degree of Mn is at least 65 %, or at least 80 %. The reduced Mn pellets may comprise 60-80 w-% Mn. Additionally, the reduced Mn pellets may comprise, for example, Fe, C, silicon (Si), sulphur (S) and phosphorus (P). The metallization degree of iron is at least 80 %, or at least 90 %. Even metallization degrees of over 85 % can be achieved for Mn, and over 90 % for Fe. However, the main advantages of the current method and reduced Mn pellets may be obtainable due to the reduction of Mn, since there is less Fe than Mn in the reduced pellets.

The reduced Mn pellets may be further processed by smelting in an electric furnace in the presence of a smelting reductant. The smelting reductant may be coke. Typically the reduced Mn pellets are combined with manganese ore and/or manganese ore sinter to obtain desired ferromanganese quality and to ascertain appropriate furnace function.

In one embodiment, the reduced Mn pellets contain 5-12 w-% carbon, or 7-11 w-% carbon or approximately 10 % carbon. The reduced Mn pellets may comprise 7.5 w-% carbon. The presence of carbon already during sintering might offer advantages in the heat distribution within the pellets, and possibly speeding up the sintering process, as the carbon provides additional energy source. This is reflected in the amount of carbon in the reduced pellets. Some of the carbon might be recovered after reduction, but also the pellets still contain an amount of carbon, which might be carried on to ferromanganese smelting.

In one aspect, use of reduced Mn pellets obtainable according to the present disclosure to produce reduced ferromanganese is disclosed.

In another aspect, a plant for producing reduced Mn pellets is disclosed. The plant is characterized in that it comprises

- a mixing station for mixing dried MnSO_4 fraction with binder to form pelletizing mixture;
- a pelletizing apparatus for pelletizing the pelletizing mixture to produce Mn pellets;
- a drying device for drying the Mn pellets;
- a sintering device for sintering the Mn pellets to produce sintered pellets; and
- a reduction station for reducing the sintered pellets to obtain reduced Mn pellets.

The plant is designed for the implementation of the method according to the present disclosure.

In one embodiment, the mixing station further comprises means for mixing carbonaceous material and/or fluxing agent with the dried MnSO_4 fraction. The mixing apparatuses may be automated and many different constructions are available in the field. The means for mixing may comprise equipment for automatic weighing and/or monitoring of the component properties.

In one embodiment, the plant further comprises calcination device, before the mixing station, or after the mixing station, or after the drying device. The positioning of the calcination device is selected
5 depending on the embodiment of the method adopted in the plant. It may be before the mixing station, meaning that the calcination device is upstream of the mixing station in the process direction. Alternatively, it may be after the mixing station. Alternatively,
10 it may be after the drying device.

In one embodiment, the drying device, the calcination device and the sintering device are arranged as one device, such as a sintering furnace comprising a plurality of process zones.

15

The mixing station and the calcination device may be operationally connected. In embodiments in which calcination takes place before mixing, the operational connection is from the calcination device towards the mixing apparatus. Conversely, in embodiments, in which mixing takes place before calcination, the operational connection is from the mixing apparatus towards the calcination device. The calcination device or the mixing station may be operationally connected to the pelletizing apparatus. The pelletizing apparatus, in turn, may be operationally connected to the drying device. The drying device may be operationally connected to the sintering device. The sintering device may be operationally connected to the reduction
20 station.
25
30

By operational connection is herein meant for example conveyer belts, screw conveyors and similar means which are known in the art and commonly employed in ore processing plants. The operational connections
35 may comprise storage bins or other storage arrangements for regulating the material flows in different parts of the plant. The operational connections be-

tween different components of the plant may be designed independently for optimal plant function.

In one embodiment, the sintering device comprises a travelling-grate sintering furnace or a steel
5 belt sintering furnace, and/or the reduction station comprises a rotary kiln or a direct reduction furnace. An example of a direct reduction furnace is a Midrex® furnace.

10 The operational connections according to the present disclosure may be configured to convey the material directly from one process step to another. Alternatively, the material may be stored between the components of the plant according to the present dis-
15 closure. Intermediate storage might be advantageous in regulating the amount of material directed to each process station. An intermediate storage may be arranged between one or more of the process stations. For example, intermediate storage can be arranged be-
20 tween the mixing station and the calcination device, or between the pelletizing apparatus and the drying device. It is possible that the intermediate storage is arranged between the sintering device and the re-
duction station or the mixing station and the
25 pelletizing apparatus. The intermediate storage may be storage bins, for example.

In one embodiment, the plant further comprises

- 30 - a leaching station for leaching manganese (Mn)-containing ore with sulphuric acid for producing manganese sulfate (MnSO_4) leachate;
- a separation station for separating MnSO_4 leachate from residual ore; and
- 35 - a MnSO_4 leachate drying station for drying the MnSO_4 leachate for producing dried MnSO_4 fraction.

The structure of the leaching station, the separation station and the MnSO_4 leachate drying station depend on the specifics of the protocol used and can vary from one embodiment to another. In one embodiment, the MnSO_4 leachate drying station comprises spray-drying equipment for spray-drying the MnSO_4 leachate.

The embodiments described hereinbefore may be used in any combination with each other. Several of the embodiments may be combined together to form a further embodiment. A method, reduced Mn pellets, their use and a plant, to which the disclosure is related, may comprise at least one of the embodiments described hereinbefore.

EXAMPLES

Reference will now be made in detail to the embodiments of the present disclosure, examples of which are illustrated in the accompanying drawings.

The description below discloses some embodiments in such a detail that a person skilled in the art is able to utilize the method, plant and the reduced Mn pellets based on this disclosure. Not all steps and features of the embodiments are discussed in detail, as many of the steps will be obvious for the person skilled in the art based on this specification.

For reasons of simplicity, item numbers will be maintained in the following exemplary embodiments in the case of repeating components.

FIGURE 1

Figure 1 illustrates a method according to one embodiment for producing reduced Mn pellets. In the embodiment of Fig. 1, the method according to the present disclosure comprises steps i) to iii), in which MnCO_3 ore is processed into dried MnSO_4 fraction,

followed by steps a) to e), in which reduced Mn pellets are produced from dried MnSO_4 fraction.

At step i), the Mn-containing ore, for example Mn carbonate ore, is leached with sulphuric acid to produce MnSO_4 leachate. At step ii), the MnSO_4 leachate is separated from residual ore. In practice, also the MnSO_4 leachate may contain solid material. The separation is typically carried out by excluding particles larger than a predetermined particle size limit. At step iii), the leachate is dried to produce a dried MnSO_4 fraction.

Steps i) to iii) are followed by step a), in which dried MnSO_4 fraction is mixed with binder, carbonaceous material and fluxing agent to produce a pelletizing mixture. Since the carbonaceous material and fluxing agent are optional constituents of the pelletizing mixture, they are depicted with dashed outline in Fig. 1. The components can be mixed in any order or simultaneously.

In the embodiment of Fig. 1, the pelletizing mixture from step a) is calcinated in step f). Calcination is an optional step and therefore marked with dashed outline in Fig. 1. Steps a) and f) are followed by step b), in which the pelletizing mixture is pelletized to produce Mn pellets. Then, the Mn pellets are dried at step c).

At step d), the dried Mn pellets are sintered to produce sintered pellets, after which step e) of reducing sintered pellets is performed and reduced Mn pellets produced.

FIGURE 2

In Figure 2, another embodiment is presented. Similar features to Fig. 1 are not repeated. In this embodiment, the process is started from dried MnSO_4 fraction obtained earlier. Further, the process is started by calcination at step f), which is performed

on dried MnSO_4 fraction before the dried MnSO_4 fraction is mixed with binder, fluxing agent and carbonaceous material in step a). Step a) is followed by pelletizing in step b), drying in step c), sintering (step d)) and reduction (step e)).

FIGURE 3

In Figure 3, another embodiment is presented. Similar features to Fig. 1 and 2 are not repeated. In this embodiment, the process is started from dried MnSO_4 fraction obtained earlier. The process starts with step a), in which binder, fluxing agent and carbonaceous material are mixed with the dried MnSO_4 fraction. This is followed by step b) of pelletizing the pelletizing mixture obtained in step a). Then, the Mn pellets are dried in step c) and calcinated in step f). The calcinated Mn pellets are sintered to obtain sintered pellets at step d), after which the sintered pellets are reduced at step e). As an end product, reduced Mn pellets are obtained.

FIGURE 4

In Fig. 4, an embodiment of a plant according to the present disclosure is presented in a schematic manner. The process steps i)-iii) and a)-e) are approximately indicated in the figure. The plant in Fig. 4 comprises equipment for producing dried MnSO_4 fraction 2, from which the reduced Mn pellets 1 are produced.

First, the plant according to the present disclosure comprises a leaching station 19 at which step i) of mixing Mn-containing ore 9 with sulphuric acid 10 is performed, to leach Mn-containing MnCO_3 ore. Although a leaching tank is depicted in Fig. 4, other types of leaching methods may be suitable. The MnSO_4 leachate 11 is then forwarded to a separation station 20 for separating MnSO_4 leachate 11 from residual ore 12 (step ii)). In Fig. 4, the method of

separation is not indicated, but it may be, for example filtration. The residual ore 12 containing, for example, impurities from ore and un-leached Mn, is lead to further processing, such as neutralization and storage, or another round of leaching. The MnSO_4 leachate 11 is directed to drying in a MnSO_4 leachate drying station 21 (step iii)) to produce dried MnSO_4 fraction 2.

The dried MnSO_4 fraction 2 is brought to a mixing station 13 to be mixed with binder 3, carbonaceous material 7 and fluxing agent 8 in order to form pelletizing mixture 4 (step a) of the method). There may be a storage and/or transportation step between the MnSO_4 leachate drying station 21 and the mixing station 13 (not depicted in the figure).

Then, pelletizing mixture 4 from the mixing station 13 is loaded into a calcination device 18. This can take place directly after mixing, or there may be intermediate storage after the mixing station 13. The treatment of the pelletizing mixture 4 in the calcination device 18 corresponds to step f) of the method according to the present disclosure.

The calcinated pelletizing mixture 4 is pelletized in a pelletizing apparatus 14 (step b)) to obtain Mn pellets 5. The pelletizing apparatus 14 may be a pelletizing drum, for example. As is known in the art, the pelletization might benefit from some amount of moisture, which may be added during the pellet formation (schematically indicated in Fig. 4 as spray). Step c) of the method is performed in a drying device 15, in which the Mn pellets 5 are dried. After drying, the Mn pellets 5 are conveyed to a sintering device 16 for sintering (step d) of the method). The resulting sintered pellets 6 are reduced at step e), which is performed at a reduction station 17, such as a rotary kiln, to obtain reduced Mn pellets 1.

FIGURE 5

In Fig. 5, an embodiment of a plant according to the present disclosure is presented in a schematic manner. The end product is reduced Mn pellets 1 which are obtained by the process according to the present disclosure. The process steps i)-iii) and f)-e) are approximately indicated in the figure. The plant in Fig. 5 comprises equipment for producing dried MnSO_4 fraction 2, from which the reduced Mn pellets 1 are produced as was described for Fig. 4.

The dried MnSO_4 fraction 2 is loaded into calcination device 18, such as a fluidized bed furnace 18. There may be a storage and/or transportation step between the MnSO_4 leachate drying station 21 and the calcination device 18 (not depicted in Fig. 5). The treatment of the dried MnSO_4 fraction 2 in the calcination device 18 corresponds to step f) of the method according to the present disclosure.

Then, the calcinated MnSO_4 fraction 2 is brought to mixing station 13 to be mixed with binder 3, carbonaceous material 7 and fluxing agent 8 in order to form pelletizing mixture 4 (step a) of the method). The pelletizing mixture 4 is pelletized in a pelletizing apparatus 14 (step b)) to obtain Mn pellets 5. The pelletizing apparatus 14 may be a pelletizing drum, for example. As is known in the art, the pelletization may benefit from some amount of moisture, which may be added during the pellet formation (schematically indicated in Fig. 5 as spray).

Step c) of the method is performed in a drying device 15, in which the Mn pellets 5 are dried. After drying, the Mn pellets 5 are conveyed to a sintering device 16 for sintering (step d) of the method). The resulting sintered pellets 6 are reduced at step e), which is performed at a reduction station 17, such as a rotary kiln to obtain reduced Mn pellets 1.

FIGURE 6

In Fig. 6, an embodiment of a plant according to the present disclosure is presented in a schematic manner. The end product is reduced Mn pellets 1 which are obtained by the process according to the present disclosure. Process steps i)-iii), as well as equipment for producing dried MnSO_4 fraction 2, are omitted for brevity, but they may be present. Steps a)-e) are schematically indicated.

In the embodiment of Fig. 6, dried MnSO_4 fraction 2 is brought to a mixing station 13 to be mixed with binder 3, carbonaceous material 7 and fluxing agent 8, in order to form pelletizing mixture 4 (step a) of the method). Then, the pelletizing mixture 4 is pelletized in a pelletizing apparatus 14 (step b)) to obtain Mn pellets 5. The pelletizing apparatus 14 may be a pelletizing drum, for example. As is known in the art, the pelletization may benefit from some amount of moisture, which may be added during the pellet formation (schematically indicated in Fig. 6 as spray).

The pelletizing apparatus 14 is operationally connected to a drying device 15 for effecting step c) of the method. The drying device 15 is operationally connected to a calcination device 18. The calcination device 18 is operationally connected to a sintering device 16. In the embodiment of Fig. 6, the drying device 15, the calcination device 18 and the sintering device 16 are constructed single furnace comprising a plurality of process zones. Examples of such devices are travelling-grate sintering furnace or a steel belt sintering furnace. The resulting sintered pellets 6 are reduced at step e), which is performed at a reduction station 17, such as a rotary kiln to obtain reduced Mn pellets 1.

EXAMPLE - Producing reduced Mn pellets

Reduced Mn pellets 1 were produced under laboratory conditions. The starting material for the method was Mn-carbonate (MnCO_3) ore 9 with the approximate composition as presented in Table 1.

5

Table 1: Chemical composition of Mn-carbonate ore

Component	Mn	Fe	SiO_2	CaO	MgO	Al_2O_3	S	CO_2
w-%	36-38	7-11	15-18	10-13	10-12	4-6	<0.5	28-30

The composition of dried MnSO_4 fraction 2 obtained after the hydrometallurgical steps i) to iii) is presented in Table 2.

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Table 2: Chemical composition of dried MnSO_4 fraction

Component	Mn	Fe	SiO_2	CaO	MgO	Al_2O_3	S	C	L.O.I	H_2O
w-%	21	1.5	0.04	0.18	4	0.83	17.4	0.08	63	23

The Mn/Fe ratio of the ore 9 was approximately 3.3 - 5.4 and thus clearly below the target value of at least 8 for successful standard ferromanganese production. After the Mn was leached from the ore 9 and dried MnSO_4 fraction 2 was produced, the Mn/Fe ratio had increased to 14.

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The dried MnSO_4 fraction 2 was crushed and ground to a grain size of below 0.5 mm. It was then calcinated at a temperature of 1,000 °C for 3 hours (step f) of the method according to the present disclosure). During calcination, air was passed through the calcination chamber.

25

After calcination, the MnSO_4 fraction was mixed with bentonite (binder) 3 and either fluxing agent (quartz) 8 or carbonaceous material 7 (coke fines) to form pelletizing mixture 4. The composition of the materials is depicted in Table 3.

30

Table 3: Properties of bentonite 3, quartz 8 and coke 7 used in the experiment. C_{fix} denotes the proportion of carbon taking part in reduction and combustion (i.e. 100% - volatiles - ash - S).

Bentonite	quartz	coke fines
water absorption value 600-650 % (ASTM standard)	grain size 80 % under 75 μ m	grain size 3-5 mm
SiO ₂ 59.5 %	SiO ₂ 95 %	C_{fix} 85 %
Na ₂ O 2.7 %	Al ₂ O ₃ 1 %	Ash 10 %
Al ₂ O ₃ 16.4 %	Fe ₂ O ₃	S 0.52 %
L.O.I. 10.8%		

5

Two batches of pelletizing mixture 4 were produced (step a) of the method). In each of them, 1 w-% of bentonite 3 was added relative to the weight of calcinated MnSO₄ fraction. In batch A, additional 3 w-% of quartz was added. In batch B, additional 3 w-% of coke 7 instead of quartz was added. The mixture 4 was thoroughly mixed for more than an hour.

The pelletizing mixture 4 was then pelletized in a laboratory-scale pelletizing disc (step b) of the method). The target diameter of the Mn pellets 5 was 12 mm. Generally, diameters of 10-12 mm were achieved. Water was manually added during pellet formation. The water content of the wet Mn pellets 5 was measured. For batch A, the moisture content was 13.6 %, and for batch B 12 %. Also the compressive strength of the Mn pellets 5 was measured. For batch A, the wet strength was sufficient ($F_{12 \text{ mm}}=1.8$ kg/pellet). For the Mn pellets 5 in batch B, the compressive strength remained low ($F_{12 \text{ mm}}=1.2$ kg/pellet). The compressive strength ($F_{12 \text{ mm}}$) was measured according to the following formula: $F_{12 \text{ mm}} = F_D \times (12.0/D)^2$. In the formula, F_D stands for the measured compressive strength (in kg), 12.0 is the target diameter of the Mn pellet 5 (in mm) and D is the measured diameter of the pellet 5 (in mm).

Preliminary test results (not shown) indicate that the inclusion of both carbonaceous material 7 and fluxing agent 8 in the pelletizing mixture 4 might improve the compressive strength of wet Mn pellets 5.

5 The pellets 5 were subsequently dried (step c) of the method) and their compressive strength was measured again. Now, the compressive strength was 26.6 kg/pellet and 23.7 kg/pellet for batches A and B, respectively. These values are clearly high enough for a
10 promising industrial-scale process. The dried Mn pellets 5 retained their round shape during drying.

Next, the obtained dried Mn pellets 5 were sintered (step d) of the method) to produce sintered pellets 6. The sintering took place a temperature of
15 1,450 °C in an induction furnace. The temperature profile of the sintering process was designed to mimic a steel belt sintering process. Air was blown into the furnace during sintering. Compressive strength of the sintered pellets 6 was measured. The values 208
20 kg/pellet and 140 kg/pellet, for batches A and B, respectively were observed, and deemed sufficient.

Finally, the sintered pellets 6 were reduced (step e) of the method) to obtain reduced Mn pellets 1. For the laboratory test, the sintered pellets 6
25 were crushed to simulate an industrial-scale process in, for example, rotary kiln. The reduction was performed in an induction furnace at a temperature of 1,300 °C or 1,350 °C. During heating and temperature maintenance phases of, the atmosphere was kept reducing (80% CO, 20% N₂) and inert during cooling (100 %
30 Ar). On industrial scale, the active regulation of the atmosphere is less important. CO gas reduces Mn during step e) of the method. To achieve an efficient process, the reduction bed comprises solid carbon, such
35 as coke. The CO₂ present in the reduction stage reacts with molecular carbon according to the Boudouard reaction to produce CO and to maintain sufficiently high

CO concentration in the material bed. Thus, with the material bed volumes of industrial scale, the reduction furnace may have an oxidizing atmosphere, since the atmosphere inside the material bed will remain reducing due to the presence of CO gas.

The furnace was charged with sintered pellets 6 and coke in 2:1 ratio. The furnace was heated at a rate of 300 °C/h, the target temperature was maintained for 1 h, after which the furnace was allowed to cool.

The reduced Mn pellets 1 contained approximately 5-7 % Fe, with a metallization degree of 93-94 %, and 60-66 % Mn, with a metallization degree of 41-89 %. The metallization degree was calculated as [metallic Fe (or Mn)/total Fe(or Mn)] × 100 %.

It is obvious to a person skilled in the art that with the advancement of technology, the basic idea of the invention may be implemented in various ways. The invention and its embodiments are thus not limited to the examples described above; instead they may vary within the scope of the claims.

CLAIMS

1. A method for producing reduced manganese (Mn) pellets (1), characterized in that the method comprises the steps of

5 a) mixing dried manganese sulfate (MnSO_4) fraction (2) with binder (3) to form a pelletizing mixture (4);

 b) pelletizing the pelletizing mixture (4) to produce Mn pellets (5);

10 c) drying the Mn pellets (5);

 d) sintering the dried Mn pellets (5) to produce sintered pellets (6); and

 e) reducing the sintered pellets (6) to obtain reduced Mn pellets (1).

15 2. The method according to claim 1, wherein carbonaceous material (7) and/or fluxing agent (8) is mixed with the dried MnSO_4 fraction (2) at step a).

 3. The method according to claim 1 or 2, wherein the method further comprises step f) of calcinating the dried MnSO_4 fraction (2) before step a), or the pelletizing mixture (4) after step a), or the Mn pellets (5) after step c).

 4. The method according to claim 3, wherein the calcination in step f) is performed in a fluidized bed furnace (18).

 5. The method according to claim 3, wherein steps c), f) and d) are performed in one device, such as a sintering furnace comprising a plurality of process zones.

30 6. The method according to any of the preceding claims, wherein the sintering in step d) is performed by travelling-grate sintering (16) or steel belt sintering (16).

 7. The method according to any of the preceding claims, wherein the sintering in step d) is performed at a temperature of at least 1,200 °C for at least 10 minutes.

8. The method according to any of the preceding claims, wherein the reduction in step e) is performed at a temperature of at least 1,200 °C, or at a temperature of 1,300 °C, or at a temperature of 1,350 °C.

9. The method according to any of the preceding claims, wherein the reduction in step e) is performed in a rotary kiln (17) or in a direct reduction furnace (17).

10. The method according to any of the preceding claims, wherein the manganese-to-iron ratio of the dried MnSO_4 fraction (2) is at least 10, or at least 12.

11. The method according to any of the preceding claims, wherein the method further comprises the steps of

i) leaching manganese (Mn)-containing MnCO_3 ore (9) with sulphuric acid (10) for producing manganese sulfate (MnSO_4) leachate (11);

ii) separating MnSO_4 leachate (11) from residual ore (12); and

iii) drying the MnSO_4 leachate for producing dried MnSO_4 fraction (2).

12. The method according to claim 11, wherein the separating in step ii) comprises filtration.

13. The method according to claim 11 or 12, wherein the drying in step iii) comprises spray drying.

14. The method according to any of claims 11 to 13, wherein the manganese-containing ore (9) comprises 30-40 w-% of elemental manganese and 5-15 w-% elemental iron (Fe).

15. Reduced Mn pellets (1) obtainable by the method according to any of the preceding claims, characterized in that the metallization degree of Mn is at least 65 %, or at least 80 %.

16. Reduced Mn pellets (1) according to claim 15, wherein the reduced Mn pellets (1) contain 5-12 w-% carbon, or 7-11 w-% carbon or approximately 10 % carbon.

5 17. Use of reduced Mn pellets according to claim 15 or 16 to produce reduced ferromanganese.

18. A plant for producing reduced Mn pellets (1), characterized in that the plant comprises

- 10 - a mixing station (13) for mixing dried MnSO_4 fraction (2) with binder (3) to form pelletizing mixture (4);
- a pelletizing apparatus (14) for pelletizing the pelletizing mixture (4) to produce Mn pellets
- 15 (5);
- a drying device (15) for drying the Mn pellets (5);
- a sintering device (16) for sintering the Mn pellets (5) to produce sintered pellets (6); and
- 20 - a reduction station (17) for reducing the sintered pellets (6) to obtain reduced Mn pellets (1).

19. The plant according to claim 18, wherein the mixing station (13) further comprises means for

25 mixing carbonaceous material (7) and/or fluxing agent (8) with the dried MnSO_4 fraction (2).

20. The plant according to claim 18 or 19, wherein the plant further comprises calcination device (18), before the mixing station (13), or after the

30 mixing station (13), or after the drying device (15).

21. The plant according to any of claims 18-20, wherein the drying device (15), the calcination device (18) and the sintering device (16) are arranged as one device, such as a sintering furnace comprising

35 a plurality of process zones.

22. The plant according to any of claims 18-21, wherein the sintering device (16) comprises a

travelling-grate sintering furnace (16) or a steel belt sintering furnace (16), and/or wherein the reduction station (17) comprises a rotary kiln (17) or a direct reduction furnace (17).

5 23. The plant according to any of claims 18-22, wherein the plant further comprises

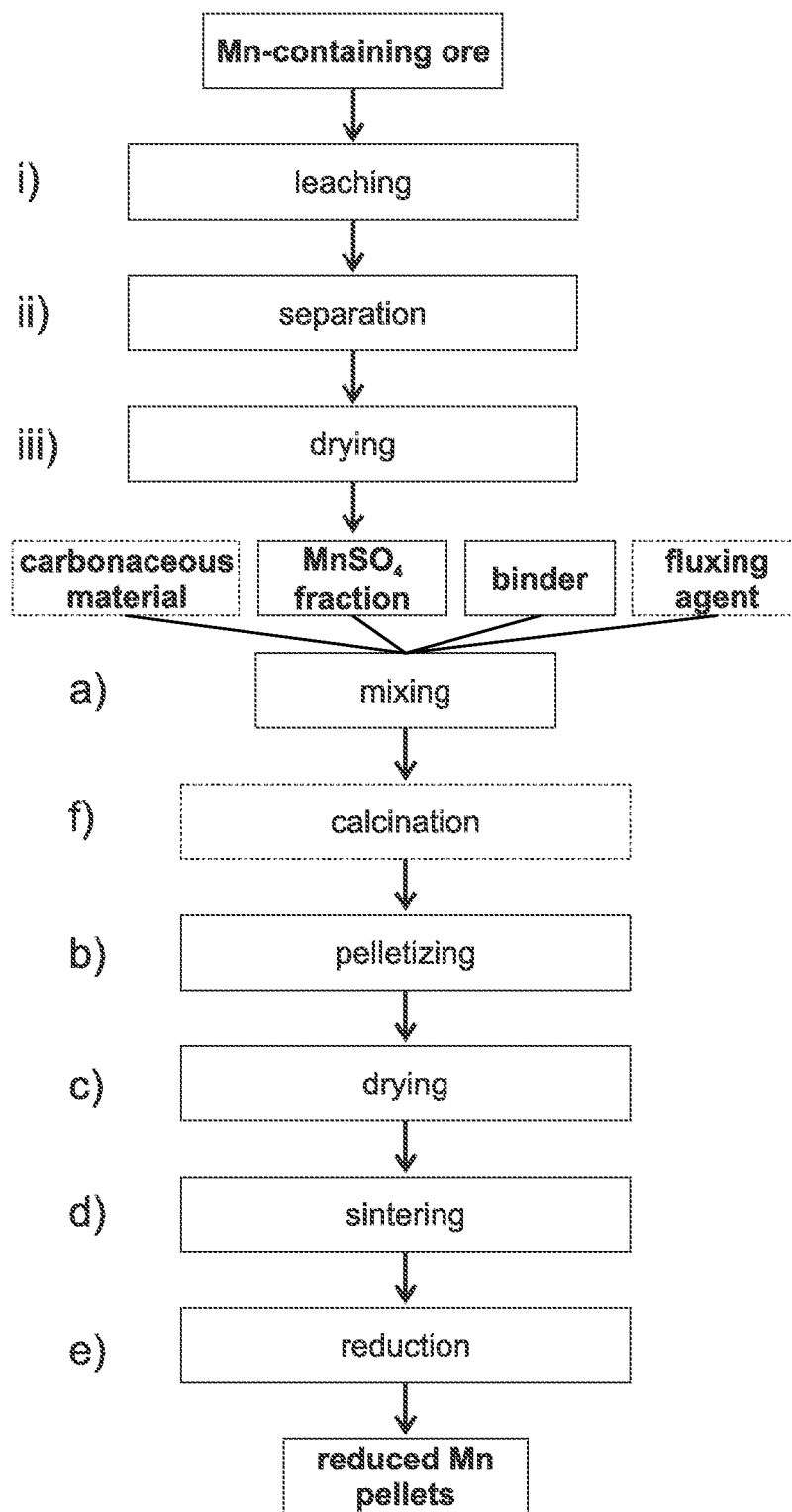
- a leaching station (19) for leaching manganese (Mn)-containing ore (9) with sulphuric acid (10) for producing manganese sulfate (MnSO_4) leachate
10 (11);
- a separation station (20) for separating MnSO_4 leachate (11) from residual ore (12); and
- a MnSO_4 leachate (11) drying station (21) for drying the MnSO_4 leachate (11) for producing dried
15 MnSO_4 fraction (2).

24. The plant according to any of claims 18-23, wherein the MnSO_4 leachate drying station (21) comprises spray-drying equipment for spray-drying the MnSO_4 leachate (11).

20

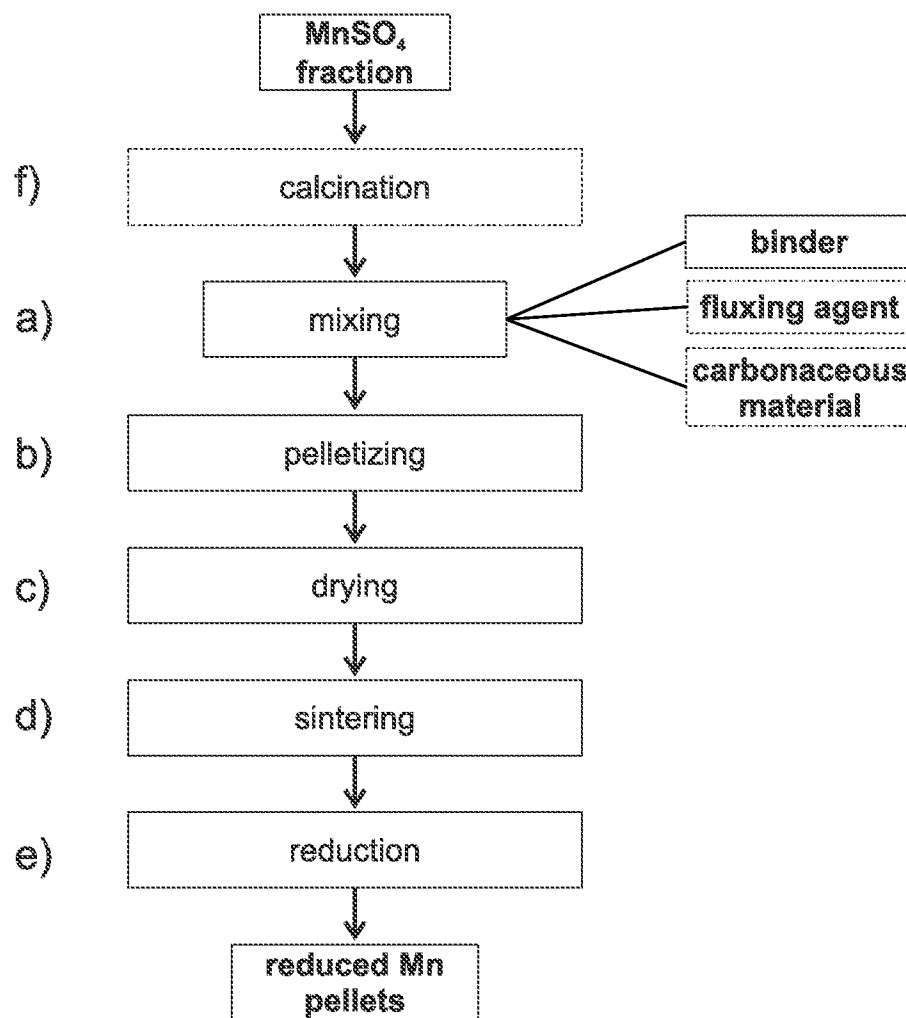
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FIG. 1



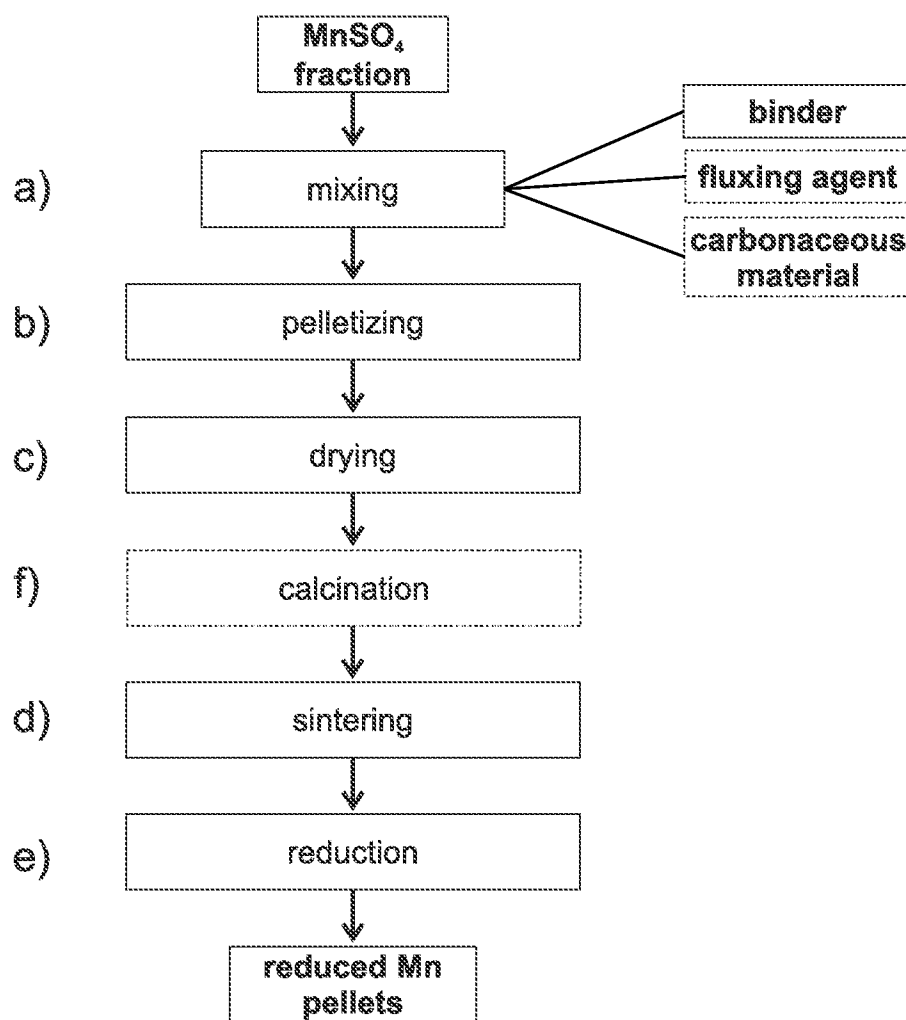
2/6

FIG. 2



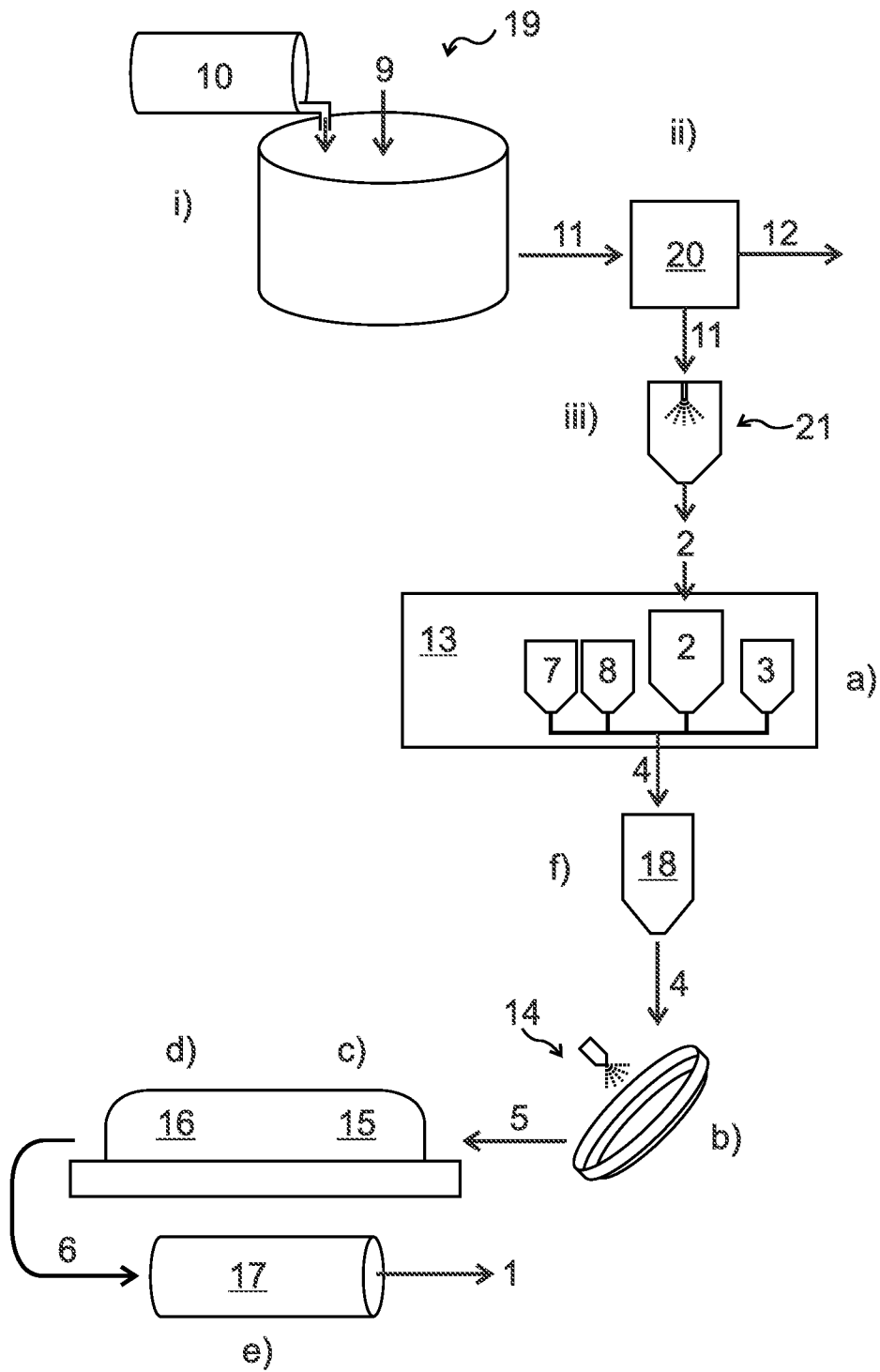
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FIG. 3



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FIG. 4



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FIG. 5

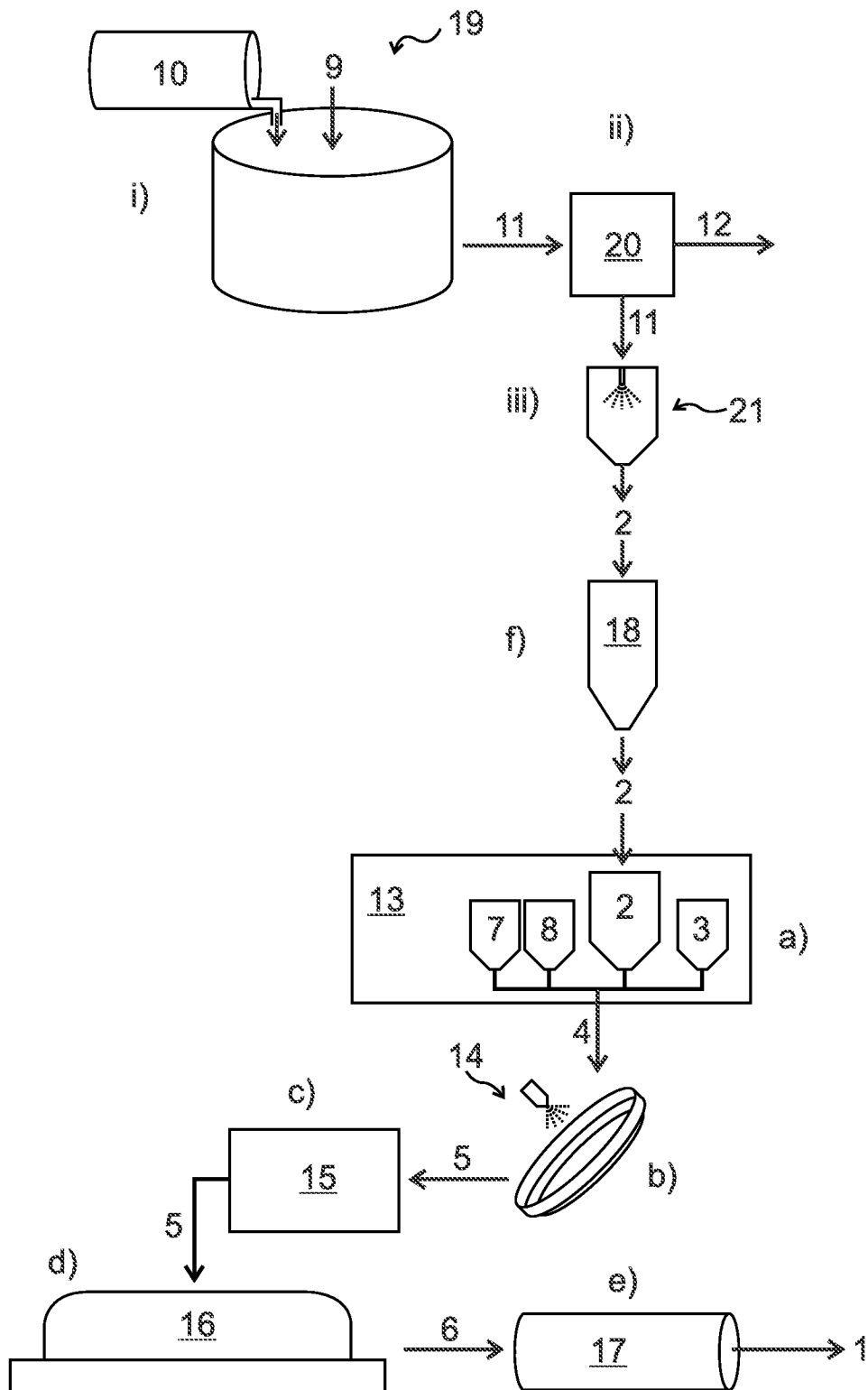
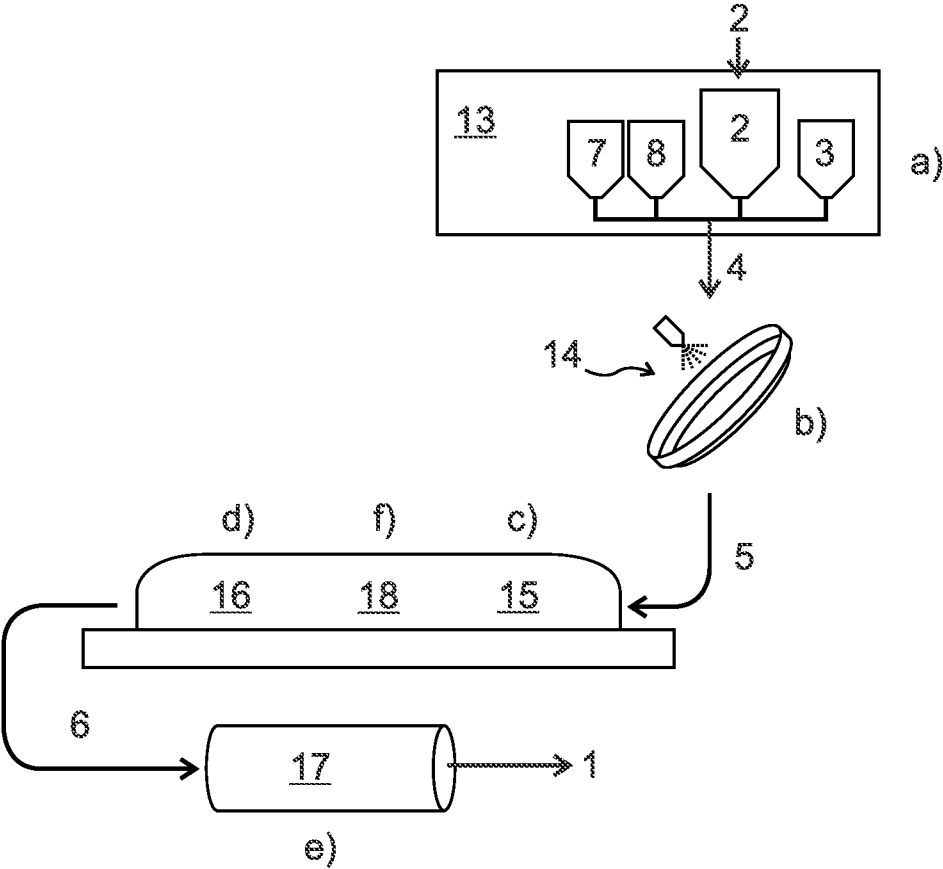


FIG. 6



INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI2016/050588

A. CLASSIFICATION OF SUBJECT MATTER

See extra sheet

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)

IPC: C22B, C01G

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

FI, SE, NO, DK

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

EPO-Internal, XPAIP, XPESP, XPIOP, XPIOPCOM, XPMISC, XPOAC, XPRD, XPTK, COMPD, INSPEC, PUBCOMP, PUBSUBS, TDB, NPL, Google

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2015092136 A1 (OUTOTEC FINLAND OY [FI]) 25 June 2015 (25.06.2015) abstract; page 2, lines 15-20; page 7, lines 1-3; claims 1, 11, 12	1-14, 18-24
Y	Lin, Q. et al. Preparation of manganese sulfate from low-grade manganese carbonate ores by sulfuric acid leaching. International Journal of Minerals, Metallurgy and Materials, vol. 23, no 5, May 2016, p. 491-500. abstract; 1. Introduction; 3.2. Purification process; 4. Conclusion; table 2	1-14, 18-24
X	JP 2001040426 A (KOBE STEEL LTD) 13 February 2001 (13.02.2001) figures 1, 2 & abstract [online] EPOQUENET EPODOC&WPI & machine translation into English [online][retrieved 8.12.2016] EPOQUENET TXPJPOEA/EPO: paragraphs [0006]-[0007], [0020]-[0021], [0025]; claim 1	15-17

☒ Further documents are listed in the continuation of Box C.
 ☒ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier application or patent but published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
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"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

09 December 2016 (09.12.2016)

Date of mailing of the international search report

13 December 2016 (13.12.2016)

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI2016/050588

C (Continuation). 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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Information on Patent Family Members

International application No.
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CLASSIFICATION OF SUBJECT MATTER

IPC

C22B 1/242 (2006.01)**C22B 1/16** (2006.01)**C22B 5/02** (2006.01)**C01G 45/10** (2006.01)**C22B 47/00** (2006.01)**C22B 1/245** (2006.01)**C22B 5/06** (2006.01)**C22B 3/08** (2006.01)**C22B 3/22** (2006.01)