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(54) METHOD FOR THE MANUFACTURE OF AGGLOMERATE CONTAINING FERROUS MATERIAL

(57) The invention relates to a method for the manufacture of an agglomerate comprising ferrous material, carbon material and fluxes, wherein a polyvinyl alcohol solution is used as a binder, as well as to the agglomerate made according to the method and the use of such an agglomerate in an iron- or steelmaking process.

The formation and chemistry of the agglomerate give rise to a three stage binding process to withstand the forces within the Blast Furnace and BOS Steelmaking process until melt out occurs.

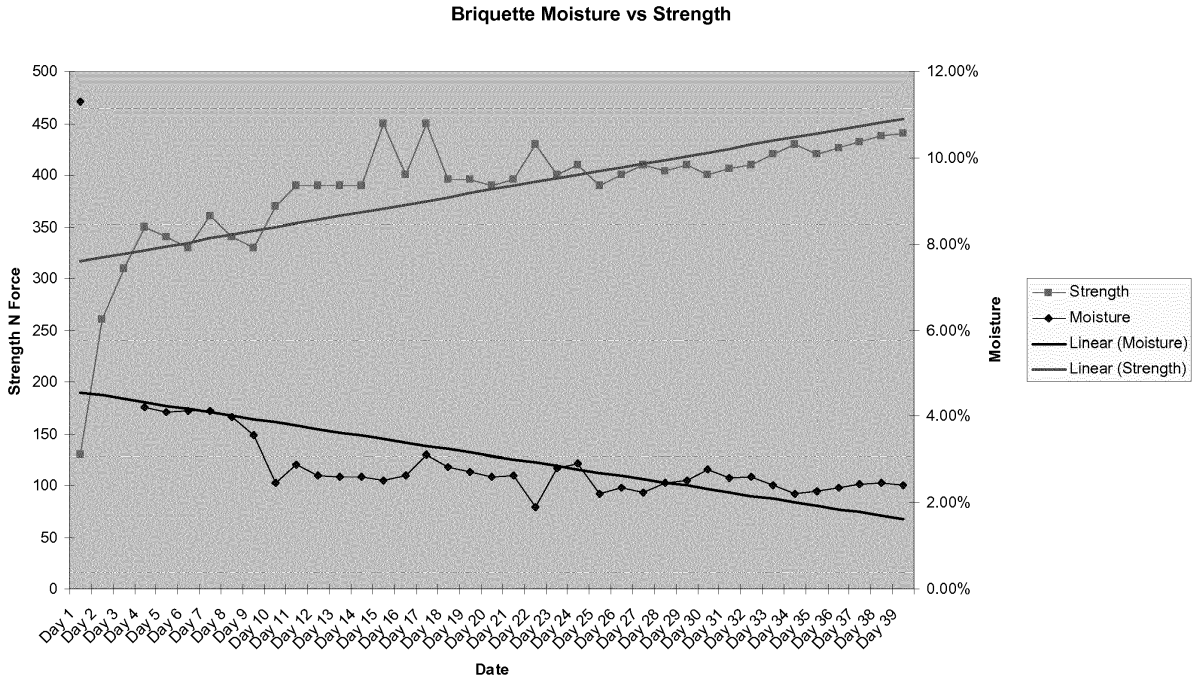

Fig.1

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Description

Field of the invention

[0001] The invention relates to a method for the manufacture of an agglomerate comprising ferrous material and carbon material, to the agglomerate made according to the method and the use of such agglomerate within a iron- or steelmaking process.

Background of the invention

[0002] In the steel industry large amounts of ferrous and carbon bearing waste products are generated in various processes, more in particular the Blast Furnace (BF) process, the Electric Arc Furnace process (EAF) and the Basic Oxygen Steelmaking (BOS) process. Most of these waste products result from the cleaning and filtering of the off gasses of these iron- and steelmaking processes.

[0003] In the past these waste products were disposed of in landfills, but because of increased environmental regulations that is no longer allowed in most countries. As a result large amounts of these waste products have accumulated over the years on the sites of steel plants.

[0004] The only feasible option is to recycle these waste products which has the advantage that pollution of the environment is prevented and that the otherwise lost ferrous and carbon material in the waste products is used in the iron- and steelmaking process.

[0005] These waste products are often fine grained and in most cases cannot directly be used in an iron- or steelmaking process. For that reason these waste products are preferably formed into an agglomerate wherein the particles forming the agglomerate are kept together by means of a binder material.

[0006] Various binder materials for such agglomerates are known in the art, for instance Portland Cement or Molasses, but these binder materials are not very suitable for recycling these waste products, because they are not mutually suitable as a binder for both BOS and BF process, specifically, in the case of Portland Cement the addition rate is such that it degrades the potential Fe content of the product entering the steelmaking process; whilst a molasses binder does not produce a product of sufficient stability under the conditions found in the blast furnace process.

Objectives of the invention

[0007] It is an objective of the present invention to provide an agglomerate containing ferrous materials which is stable up to high temperature under both oxidising and reducing conditions.

[0008] It is another objective of the present invention to provide an agglomerate containing ferrous materials of high compressive strength.

[0009] It is another objective of the present invention to provide a method to manufacture such an agglomerate containing ferrous materials.

[0010] It is another objective of the present invention to provide a method to manufacture an agglomerate containing ferrous materials from which the zinc content is removed.

[0011] It is still another objective of the present invention to provide a method to manufacture an agglomerate by using ferrous waste products from the iron- and steelmaking processes.

Description of the invention

[0012] According to a first aspect of the invention one or more of the objectives of the invention are realized by providing a method for the manufacture of an agglomerate comprising a ferrous material, a carbon material and a binder, wherein the method comprises the steps of:

- providing a binder by preparing an aqueous solution of polyvinyl-alcohol (PVA),
- mixing the aqueous solution of PVA with the ferrous material and the carbon material,
- forming the agglomerate, and
- curing the agglomerate.

[0013] The term ferrous materials as used in the description and claims comprises iron containing waste materials with a minimum content of 20 wt% iron and/or iron ore and which may contain various other metals and metal-oxides.

[0014] The term carbon materials as used in the description and claims comprises carbon containing waste materials, graphite and/or cokes.

[0015] The term "agglomerate" as used in the description and claims shall mean "briquette" or "pellet" as the case may be.

[0016] The term "briquette" as used in the description and claims comprises all methods of forming an agglomerate of ferrous and carbon mineral using roller presses, die presses (including die variants such as rotating table presses) as well as extrusion or pellet production using a pan or disc pelletiser.

[0017] The PVA used for this process is commercially available in powder form and covers all suitable grades that would be considered as being in the medium viscosity range and which are soluble in water. The PVA chain may be in various degrees of saturation with OH groups but typically saturation levels from 80% to fully hydrolysed are employed.

[0018] A solution of the polymer is made by heating water to near boiling temperature, adding the PVA and preparing an aqueous solution of PVA comprising 5 - 20 wt% PVA, more preferably comprising 8 - 12 wt% PVA. The width of the wt% range depends on actual grade of polymer and viscosity. The bonding process employs the binder addition of the aqueous solution of PVA to the materials comprised in the agglomerate, wherein the agglomerate before forming contains an amount of dry PVA

in the range 0.1 -1.2 wt% of the total weight of the agglomerate, that is of the final mix of all materials constituting the agglomerate. Preferably, the agglomerate before forming contains an amount of dry PVA in the range 0.2 -0.8 wt% of the total weight of the agglomerate

[0019] According to a further aspect of the invention MgO-containing fluxes and/or CaO-containing fluxes are added to the agglomerate. These fluxes are used to control different stages in the forming and curing of the agglomerate and also in the use of the agglomerate in the iron- and steelmaking process. Addition of CaO in the mix can increase the degree of -OH saturation within the PVA molecule.

[0020] Preferably the materials of the agglomerate are mixed prior to adding and mixing with the aqueous solution of PVA in order to first get a homogeneous mixture before binding the different particles of the agglomerate.

[0021] The moisture content of the agglomerate needs to be controlled in order to form a briquette or pellet with sufficient green strength for handling the agglomerate prior to the curing thereof. The optimum moisture content in the briquette being bound is a function of granularity, applied pressure and the method of forming e.g. roll briquetting, extrusion or pellet formation. There are two optimum moisture considerations; one is related to green strength of the briquette on formation and the other to final developed cured strength. According to a further aspect of the invention the moisture content of the agglomerate after curing is in the range of 1 - 6 wt%, preferably in the range of 1 - 4 wt%.

[0022] Low level heat is beneficial in the curing process (rate of gain of strength) which can be obtained by mixing ferrous material in the form of filter cake from the BOS process which contains iron oxides in a low oxidation state whereby on further oxidation the reaction is strongly exothermic. In order to control the rate of heating, the BOS cake is pre-blended with other thermally stable ferrous dusts, which absorb the excess heat and raise the overall temperature of the mix used in the agglomeration process

[0023] Final trimming of moisture to the point required to form the agglomerate is by addition of moisture or by small additions of in particular burnt lime (CaO) at the mixing stage prior to binder addition, which on hydration is also exothermic further aiding drying.

[0024] According to a further aspect of the invention the curing time of the agglomerate is shortened by heating the agglomerate to a temperature in the range 100 - 150°C.

[0025] The granularity of the ferrous, carbon and flux materials is important and for that reason it is provided that the ferrous, carbon and/or flux materials have a grain size $\leq$ 5.0 mm. Preferably it is provided that at least 50% of the grains is $\leq$ 1.0 mm, and more preferably that at least 67% of the grains is $\leq$ 1.0 mm.

[0026] The method according to the invention allows for the use of ferrous and carbon bearing wastes from the iron and steel industry to be re-utilised and recycled within the BF and BOS processes. The basis for the mix of materials that can be recycled are BOS and BF filter cakes from the off gas cleaning systems. Prime ores and coals can also be used, in particular milled ore concentrates. The method also provides a route for the use of materials of poor sintering quality, or that are environmentally deleterious to the traditional sinter plant route, as such the method offers a potential alternative to sintering or indeed potentially conventional pelletising processes. Additional materials such as mill scales, fine grindings from other processes can be added to the base materials to control the ferrous content of the cold bound material. Providing the ferrous material, carbon material, fluxes and binder and the subsequent mixing, forming and curing of the agglomerate is the first stage in the method.

[0027] The first stage takes place as the briquettes or pellets are cured and involve the -OH groups on the polymer chain being attracted to other -OH groups on adjacent molecules or to the surface of the particles being bound. Although the bonding forces are described as "weak hydrogen bonding" this imparts very high cold compressive strength to the briquettes. As the molecular chain lengths of the PVA are very long the OH groups present form a three dimensional matrix with intermolecular binding and molecular to particle binding.

[0028] According to a further aspect of the invention a cross-linking agent may be added during the formulation of the aqueous polymer solution to promote cross-linking of the PVA to further improve the bonding forces between the polymer chains. A possible cross-linking agent that can be used is for instance Gluteraldehyde.

[0029] In the second stage of the process the temperature is elevated to the decomposition temperature of the PVA at circa 200°C. As the temperature increases between 200 and 450°C OH-groups are stripped from the polymer chain length producing polyenes. Free radical reactions then take place and it is at this stage that multi-valent metal ions present in the ferrous waste streams previously mentioned are believed to act as catalysts in the chain-scission and aromatic compound formation producing oligomers present as char products. It is also believed that the elemental carbon present in the agglomerate material being bound also takes part to a greater or lesser degree in the complex organic chemistry making up the formation of the oligomer char products. The oligomer char products then form a thermally stable binding mechanism that is stable up to ~880-900°C at which point the matrix breaks down and the carbon is "burnt out.

[0030] The second stage of the process takes place either during use of the agglomerate in a BF or BOS process or potentially within a thermal pre-treatment process .

[0031] Recycling of ferrous waste material containing Zn and/or alkali metals imposes challenges in terms of productivity and efficiency at the blast furnace, therefore to adopt the blast furnace recycle route for such materials

the agglomerate is preferably subjected to a thermal pre-treatment process to reduce/remove the Zn/alkali metals in the agglomerate. In the thermal pre-treatment process the agglomerates are heated up to a temperature of about 1100°C as a result of which the Zn and/or alkali metals vaporize and can subsequently be collected from the off gas. By pre-treatment In this manner vaporization of the Zn and/or alkali metals in the BF or BOS process, can be minimised reducing the detrimental effects in the BF process. Such a thermal pre-treatment process could be carried out in for instance a tunnel furnace or kiln.

[0032] In the third stage reduction takes place in the outer shell of the briquette forming a sintered hardened shell. This stage can be made to start before the second stage binding has failed. This is a function of the very fine iron oxide and carbon (micron particulates) that are present in the agglomerate formulation. Within the BF process the reducing atmosphere encourages reduction within the outer shell of the briquette causing the formation of "spongy iron" which then continues to bind the briquette until the briquette becomes plastic as it reaches the melting zone within the furnace, where the flux addition aids final melt-out. This behaviour is demonstrated by briquettes which were charged to and subsequently recovered from the stack and cohesive zone of an experimental blast furnace used widely to test the behaviour of other burden materials.

[0033] According to a further aspect of the invention the agglomerates are made partially self-reducing, for which it is provided that the amount of carbon material is $\geq$ 5 wt% of the total weight of the agglomerate. However, if the carbon levels are lifted to about 8 - 12 wt%, the briquettes have excellent self reducing properties where it can be shown that all the carbon and the polymer is consumed. This has been shown to give a metallization level of ~30% which gives the briquettes very high strength.

[0034] In the BF process, the combination of the polymer and the selected blend of materials in the briquette enable the swelling forces on reduction of iron oxides to be overcome, thus allowing the briquette or pellet to reach the plastic or melting zone without significant degradation. In the BOS process the combination of the polymer and the selected blend of materials in the briquette preserves the briquette integrity on addition to the bath slowing down the reaction of the briquette or pellet, preventing overspill at the vessel.

Brief description of the drawings

[0035] The invention will be further explained by way of the examples shown in the drawings, in which:

- fig.1 shows a graph with the moisture content against the strength of an agglomerate on curing,
- fig.2 shows a graph with particle size distribution of the materials making up an agglomerate in the sub 1.0mm range,
- fig.3 shows examples of a number of waste materials that can be used in the manufacturing of the agglomerates,
- fig.4 shows an image of Zn crystals formed on the surface of a briquette,
- fig.5 shows a table with the chemical composition of a briquette before and after heat treatment to remove Zn and/or alkali metals,
- fig.6 shows the structure of a briquette before a BF temperature/reduction simulation test,
- fig.7 shows the structure of a briquette after a BF temperature/reduction simulation test,
- fig.8a shows briquettes recovered from the Experimental Blast Furnace Upper Stack after nitrogen quenching,
- fig.8b shows briquettes recovered from the Experimental Blast Furnace Mid Stack after nitrogen quenching, and
- fig.8c shows briquettes recovered from close to the Experimental Blast Furnace cohesive zone after nitrogen quenching.

Detailed description of the drawings

[0036] Fig.1 shows the relationship between the briquette moisture content on curing and strength, wherein the lower line and curve represent the moisture content and the upper line and curve the compressive strength. Drying out of the briquette increases cold compressive strength over time. Heat can be applied that will increase the rate of gain in strength, reducing the curing time and hence stock at the production unit prior to use. Retained heat is preferable as this further aids curing and attainment of final strength of the briquette.

[0037] Fig.2 shows a graph of the sub 1.0 mm size distribution of the base material used for agglomeration obtained after screening the sample down to this size fraction. This fraction represented 67% of the whole with the balance (33%) in the size range 1.0 - 5.0mm. The sub-millimetre size fraction is important in the reduction of the outer shell of the agglomerate, which results in the forming of a sintered hardened shell and therewith in an increased compressive strength of the agglomerate.

[0038] Fig.3 shows a table with the composition of a number of waste materials that can be employed in the manufacture of the briquettes as examples of typical arising ferrous and carbon bearing waste materials from iron- and steelmaking processes. The chemical analysis is by means of X-ray fluorescence.

[0039] Occurring within the waste iron oxide materials from the BOS plant and BF plant are small amounts of multi-valent metal ions such as vanadium, chromium, (as well as iron itself), and pseudo metal ions such as phosphorus which can act as catalysts within the second stage of the binding process as temperatures are elevated between ~200°C and ~450°C.

[0040] The method according to the invention, whilst

being able to make use of prime iron ores and coals, is principally aimed at the recovery and re-use of waste products being generated in the Iron and Steel works, not being confined to just off gas dusts filtered from the BF and BOS processes but also filtered dusts from sinter plants, EAF processes, de-sulphurisation stations and other filtration processes for environmental control.

[0041] In oxidising conditions the briquettes are thermally stable as was demonstrated by placing briquettes in a muffle furnace and heating these up to 1400°C. The briquettes are partially self reducing even with as little as 5% carbon in the briquette composition. However, if the carbon levels are lifted to ~10%, the briquettes have excellent self reducing properties where it can be shown that all the carbon and the polymer is consumed. This will give a metallization level of ~30% which gives the briquettes very high strength.

[0042] Fig. 4 shows an image taken of the surface of a briquette after heating to 1000°C for an hour, zinc crystals are seen as a white growth on the surface of the briquette, analysis shows these to be 95% Zinc.

[0043] Fig. 5 shows a table of the analysis of a briquette before and after being heated to 1100°C, again for an hour. The table shows that the zinc fully volatilises and is completely removed from the briquette.

[0044] Fig. 6 shows the microstructure of a briquette, before metallurgical testing,the structure is made up of amorphous carbon, iron oxide and cementite. After testing under conditions simulating the blast furnace stack, these particles are then reduced becoming much coarser in microstructure giving a spongy network of iron, wustite and slag phases.

[0045] Fig. 7 shows the microstructure of a briquette after the aforementioned test, the spongy iron is seen as the white inter grown particles.

[0046] Fig. 8a shows the condition of briquettes recovered from the upper layers of the experimental blast furnace stack (EBF) after nitrogen quenching. The briquettes were found to exhibit the as charged condition with only early evidence of the reduction process. The image shows no evidence of fracturing, or that the integrity of the briquette is compromised, at this early stage as a result of heating or reduction.

[0047] Fig. 8b shows the condition of briquettes recovered from layers within the mid stack region of the EBF stack after nitrogen quenching. The briquettes were found to exhibit evidence of reduction and early signs of softening (the marks on the surface of the briquettes are impressions from the wire basket in which they were contained when charged to the EBF). The image again shows no evidence of fracturing, or that the integrity of the briquette is compromised at this stage of the briquettes transit through the furnace as a result of heating or reduction.

[0048] Fig. 8c shows the condition of briquettes recovered from layers close to the cohesive zone of the EBF stack after nitrogen quenching. The briquettes show clear evidence of reduction and a degree of metallization (as indicated by the lighter grey coloration). The briquettes have clearly softened to the point where the briquettes themselves have become agglomerated and co-joined. The wire marks from the baskets in which they were charged to the EBF can be clearly seen. The image again shows no evidence of fracturing, or that that the integrity of the briquette is compromised, other than softening and metallization, as a result of heating or reduction. It was not possible to demonstrate the final stage in the EBF where full reduction and melt out occurred with separation of the metal and slag phases other than to state below the cohesive zone there were no briquettes evidenced.

Claims

1. Method for the manufacture of an agglomerate comprising a ferrous material, a carbon material and a binder, wherein the method comprises the steps of:

   - providing a binder by preparing an aqueous solution of polyvinyl-alcohol (PVA),
   - mixing the aqueous solution of PVA with the ferrous material and the carbon material,
   - forming the agglomerate, and
   - curing the agglomerate.

2. Method according to claim 1, wherein MgO-containing fluxes and/or CaO-containing fluxes are added to the agglomerate.

3. Method according to claim 1 or 2, wherein the materials of the agglomerate are mixed prior to adding and mixing with the aqueous solution of PVA.

4. Method according to one or more of claims 1-3, wherein the aqueous solution of PVA comprises 5 - 20 wt% PVA.

5. Method according to one or more of claims 1-4, wherein the agglomerate before forming contains an amount of dry PVA in the range 0.1 -1.2 wt% of the total weight of the agglomerate.

6. Method according to one or more of claims 1-5, wherein the agglomerate before forming contains an amount of dry PVA in the range 0.2 -0.8 wt% of the total weight of the agglomerate.

7. Method according to one or more of claims 1-6, wherein a cross-linking agent is added for cross-linking the PVA.

8. Method according to one or more of claims 1-7, wherein the ferrous and/or carbon material have a grain size $\leq$ 5.0 mm.

9. Method according to claim 8, wherein at least 50%

of the grains is ≤ 1.0 mm.

10. Method according to one or more of claims 1-10, wherein the amount of carbon material is ≥ 5 wt% of the total weight of the agglomerate.

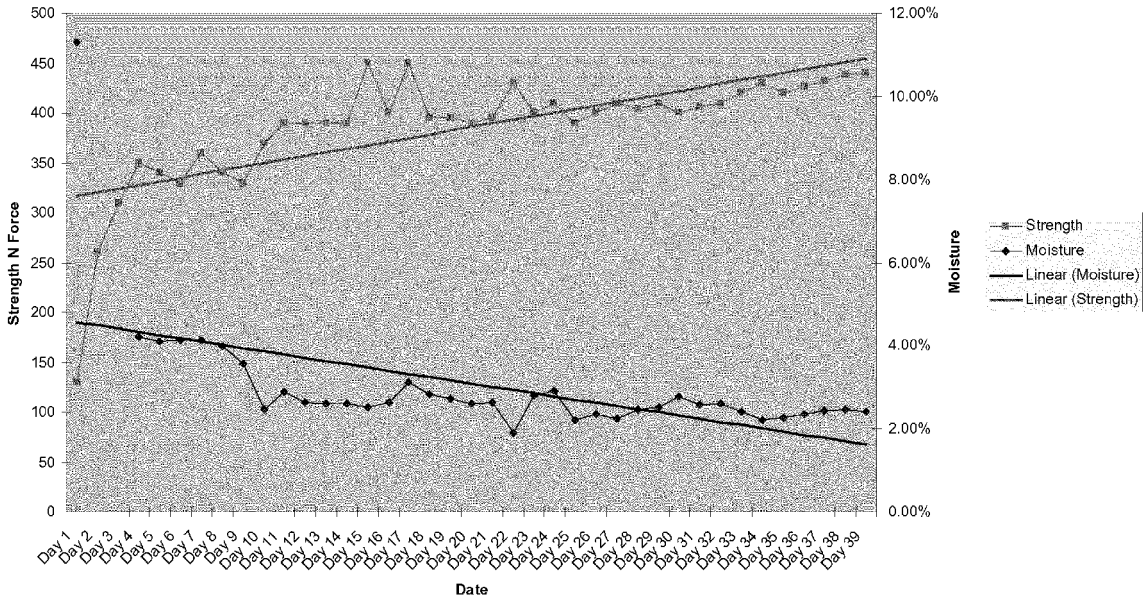
11. Method according to one or more of claims 1-11, wherein the agglomerate is cured by heating the agglomerate to a temperature in a range from 100°C to 150°C.

12. Method according to one or more of claims 1-11, wherein the moisture content of the agglomerate after curing is in the range of 1 - 6 wt%.

13. Method according to one or more of claims 1-12, wherein the agglomerate is subjected to a thermal pre-treatment process in order to remove Zn and/or alkali metals from the agglomerate.

14. Agglomerate obtained by the method according to one or more of claims 1-13.

15. Use of the agglomerate according to one or more of claims 1-14, wherein the agglomerate is used in an iron- or steelmaking process.


Strength N Force
Moisture
Date
Strength
Moisture
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450
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200
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Day 39

Fig.1

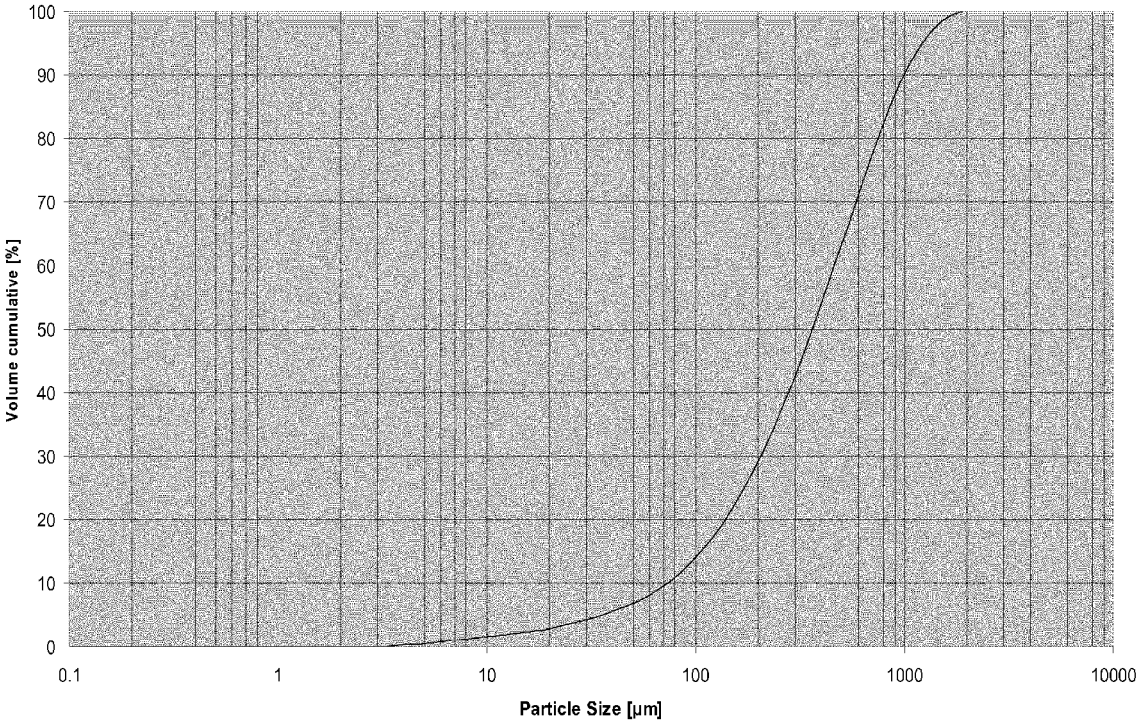

100
90
80
70
60
50
40
30
20
10
0
Volume cumulative [%]
0.1
1
10
100
1000
10000
Particle Size [µm]

Fig.2

Component	Fe	CaO	SiO2	MnO	AL2O3	MgO	P2O5	K2O	TiO2	Na2)	Cr2O3	C	S
Units	%	%	%	%	%	%	%	%	%	%	%	%	%
Analysis Method	XRF	XRF	XRF	XRF	XRF	XRF	XRF	XRF	XRF	XRF	XRF	CA	CA
Example 1	20	6.1	8.8	11	0.98	28	0.07	3.4	0.01	2.6	0.12	1.3	1.22
Example 2	70	0.09	0.66	0.53	0.18	0.11	0.14	0.34	0.02	<0.08	0.02	0.4	0.27
Example 3	63	6.6	1.4	1.5	0.18	1.33	0.13	0.24	0.02	0.09	0.07	2	0.14
Example 4	71	0.36	0.44	1.1	0.24	0.13	0.06	<0.03	<0.01	<0.06	0.25	1.5	0.13
Example 5	39	12.9	9.5	16	0.97	3.57	0.2	0.39	0.11	0.17	0.12	2	0.39
Example 6	67	6.1	1.3	1.8	0.1	1.13	0.17	0.09	0.02	<0.08	0.05	1.1	0.08
Example 7	28	28.6	1.4	0.26	0.24	2.82	0.07	5.9	0.05	1.3	0.02	11.1	1.57
Example 8	45	10.5	6.3	0.56	1.7	2.01	0.1	1.5	0.12	0.16	0.04	6.1	0.55
Example 9	35.6	3.6	6	0.31	1.9	1.17	0.08	0.22	0.12	0.08	n/m	35.7	0.27
Example 10	55	4.7	2.3	1.3	0.57	1.18	0.16	0.13	0.05	0.29	n/m	7.2	0.2

Waste materials that can be used in the manufacture of the agglomerate

Fig.3

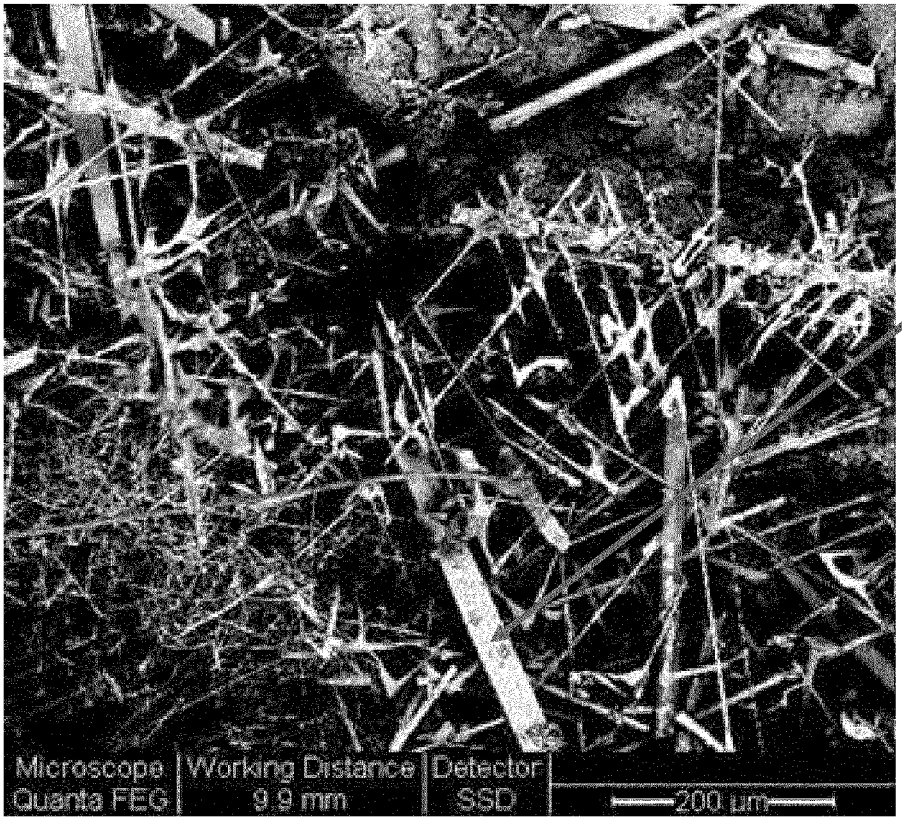
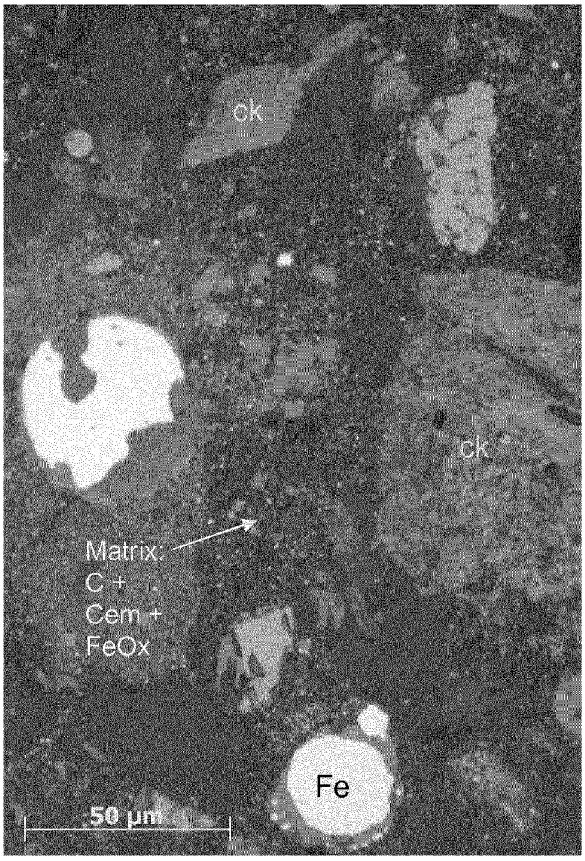

95% Zinc
Microscope
Quanta FEG
Working Distance
9.9 mm
Detector
SSD
200 µm

Fig.4

Component	Unit	Briquettes before Pre-Treatment	Briquettes after Pre-Treament
Fe	%	53.2	68.6
Fe2O3	%	75.9	0
FeO	%	0.14	61.1
Metalic Iron	%	0	21.1
CaO	%	4.67	6.02
SiO2	%	4.86	6.26
MnO	%	1.31	1.69
Al2O3	%	0.65	0.84
MgO	%	1.72	2.21
P2O5	%	0.09	0.12
K2O	%	0.21	0.26
TiO2	%	0.02	0.02
Na2O	%	0.07	0.1
Cr2O3	%	0.06	0.07
BaO	%	0.04	0.05
ZrO2	%	0.02	0.02
Zn	%	0.28	0
Pb	%	0.15	0
V2O5	%	0.04	0.05
Sr	%	0.01	0.01
Ni	%	0.02	0.02
Cu	%	0.02	0.02
C	%	9.21	0
PVA	%	0.5	0

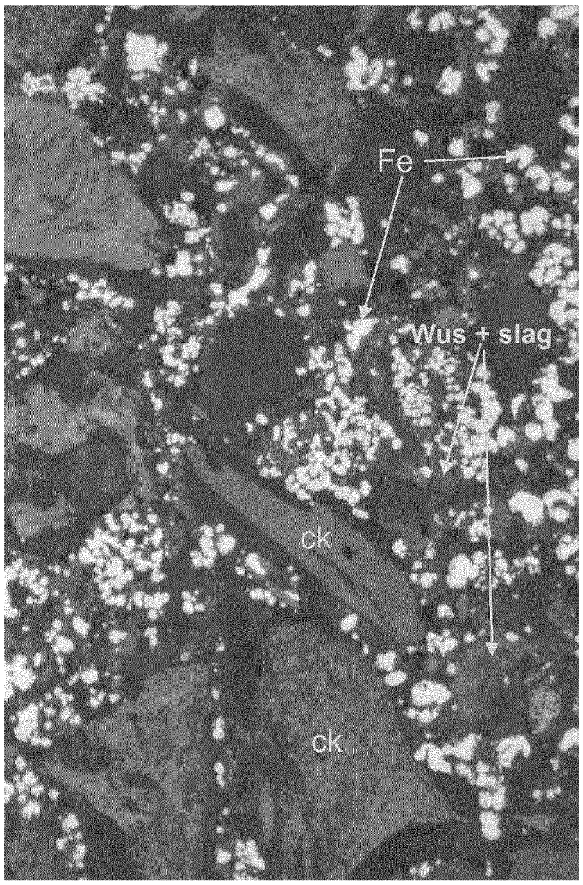
Fig.5



Extremely fine grained matrix of Carbon (Amorphos), Cementite and Iron Oxide

Larger particles of Coke (ck) can also be seen along with some larger metallic particles (Fe).

Fig.6



Previous matrix shown in Fig 6 now heavily reduced and converted into Sponge like Matrix of Metallic Fe, Wustite and Traces of Slag

Fig.7

Fig.8a.

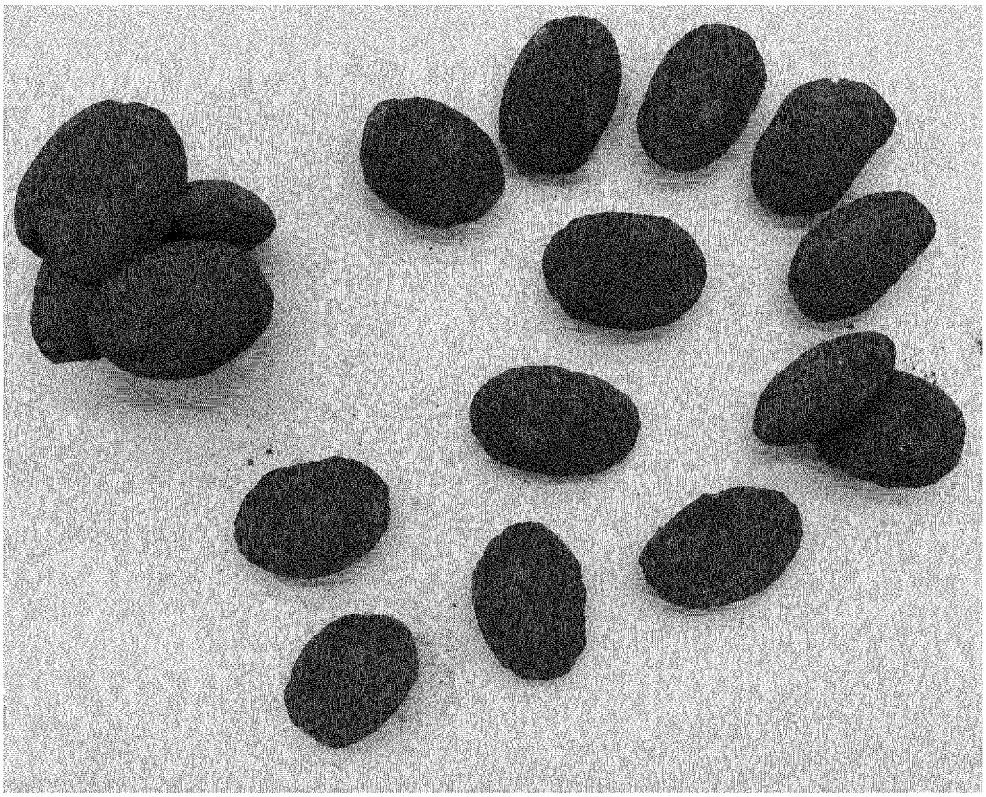


Fig.8b

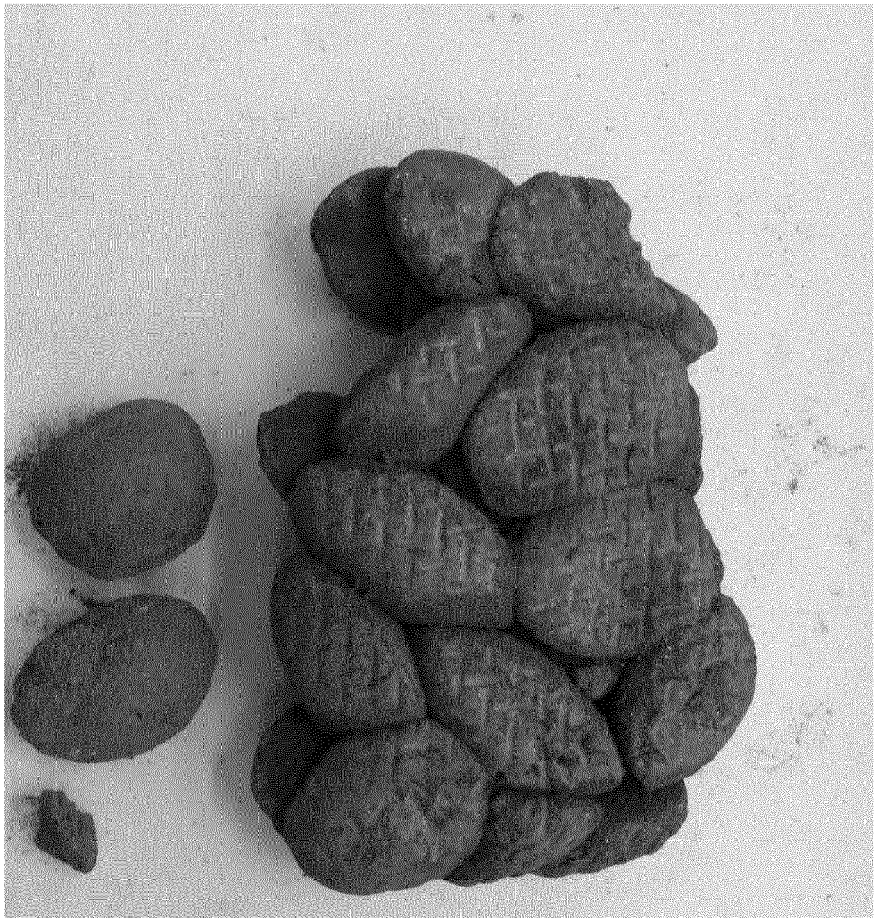


Fig.8c.

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EUROPEAN SEARCH REPORT

Application Number
EP 15 02 0131

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	US 5 589 118 A (FORD JR GEORGE W [US] ET AL) 31 December 1996 (1996-12-31) * the whole document *	1-15	INV. C22B1/243 C22B1/245
X	US 6 384 126 B1 (PIRTLE JAMES [US] ET AL) 7 May 2002 (2002-05-07) * the whole document *	1-15	
X	JP 2003 247026 A (NISSHIN STEEL CO LTD) 5 September 2003 (2003-09-05) * the whole document *	1-15	
X	CN 103 276 203 B (JIAYUGUAN DAYOU ENTPR COMPANY) 29 October 2014 (2014-10-29) * the whole document *	1-15	

TECHNICAL FIELDS SEARCHED (IPC)

C22B

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	11 January 2016	Juhart, Matjaz

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 15 02 0131

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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11-01-2016

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