### European Patent Specification

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**Process for treating of flue dusts from electric steelworks**

Verfahren zum Behandeln von Flugstäuben aus Elektrostahlwerken

Procédé pour traiter des poussières émanant d’aciéries électriques

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Description

[0001] It is well-known that iron scrap smelting in electrical furnace causes 10-20 kg of dust to be formed per each ton of produced steel. This lightweight, fine and easily dispersible dust (referred to as "EAF") contains, as their oxides, 20-25% Fe, 18-25% Zn, 2-4% Pb, and still other, more or less dangerous, impurities.

[0002] On considering the size of present steelworks, the produced amount of dusts is extremely large and, owing to health, environmental and economic reasons, a process of inertization and recovery of valuable metals is urgently required.

[0003] The first solution attempted was of recycling the dust to the same furnace which produces it. By this way, iron can be recovered and oxides of non-ferrous metals can be gradually concentrated in the fumes, but greater difficulties were soon experienced in the steelworks, in furnace charging and fumes collection, the energy consumptions resulted to be higher, and the throughput of furnaces decreased, so the method is regarded as not being desirable for economic and, above all, environmental, reasons.

[0004] At present, for processing EAF dusts several thermal processes in reducing environment are used, and are carried out in rotary furnaces, hearth furnaces, plasma furnaces and flame furnaces.

[0005] The most widely known and diffused process is the Waelz-Berzelius process in which the dusts are mixed with fine coal, lime and silica and the resulting mixture is fed to a long rotary furnace.

[0006] The reduction takes place in that portion of the furnace in which temperatures of 1400°C are reached: FeO is not reduced and turns into slag. Also Inmetco process (USA) is preferably used for processing the dusts from stainless steel producing electrical furnaces used to produce stainless steel.

[0007] Zn and Pb in Waelz oxides reach concentration levels of 60% and, respectively, 10%; therefore, this material is suitable for recovering both metals.

[0008] HTR process, conceptually similar to the preceding one, achieves a certain energy saving by feeding the dust to that portion of the furnace in which temperatures of 1400°C are reached: FeO is not reduced and turns into slag.

[0009] Plasmadust process (Sweden) uses a non-transferred arc plasma, causing a gas to flow through the electric arc discharge kept burning between two electrodes installed inside the tuyères of a metallurgical furnace top fed with coke flowing from top downwards. The pelletized dusts with coal and flux are injected to the flame of plasma torch. Iron oxides are reduced to cast iron, Zn and Pb are reduced and volatilized, and are collected in an outer condenser. Lime and silica react with the other dust components, turning them into slag. At present, this process is mainly used for processing the dusts from electrical furnaces used to produce stainless steel.

[0010] Also Inmetco process (USA) is preferably used for processing the dusts from stainless steel producing electrical furnaces. A rotary table furnace is used inside which the mixture of dust with coal and fine coke, pelletized, is submitted to a first reduction: Zn and Pb concentrate in the fumes from this furnace. The pre-reduced pellets which contain all iron are charged, together with scrap and rolling scales to a submersed arc electrical furnace to obtain an iron alloy with Cr, Ni and Mo contained in the original dusts.

[0011] St. Joe reactor is a vertical steel furnace with water jacket subdivided into 2 steps. The burner, fed with coke powder, is fed with oxygen enriched air, so a particularly high-temperature flame is generated (approximately at 2000°C), the metallurgical charge is pneumatically injected to the reducing region of the flame. Zn, Pb and Cd are reduced, vapourized, and collected in a sock filter.

[0012] The high-iron slag is granulated and can be sold to cement factories (in order to add iron to cement mix), or is used as raw material for blast furnaces.

[0013] Tetronics process by British Steel Co. uses a transferred-arc plasma furnace. The plasma torch is installed on furnace crown and, in order to distribute energy to the bath, it can rotate with a variable inclination to the vertical axis.

[0014] The fumes from stainless steel, mixed with 28% of anthracite are continuously fed to the furnace (with a feed rate of 500 kg/h) at a constant temperature of about 2000°C. Cr, Ni, Mo are recovered as iron alloys.

[0015] The exhaust gases are deprived of dusts inside sock filters.

[0016] Tetronics process by British Steel Co. uses a transferred-arc plasma furnace. The plasma torch is installed on furnace crown and, in order to distribute energy to the bath, it can rotate with a variable inclination to the vertical axis.

[0017] Also EAF dusts containing 18% of Zn were tested, with ZnO concentration up to 60% being obtained.

[0018] Also Kaldo process for Boliden, developed for lead bearing residues, and the Slag Fuming process, very well-known for Zn and Pb recovery from silica slag from wind furnace, can be regarded as representing a possible solution for EAF dusts processing.

[0019] In the vertical electrothermic furnace developed by St. Joe Minerals, studied for zinc minerals, EAF dusts may be charged, and sintered them with the residue from blends roasting.

[0020] The resulting sintered product flows then through a pre-heating rotary furnace and then enters the electrothermic furnace from top. The coke feeds the furnace with energy and creates a conductive region for electrical energy supplied by means of graphite electrodes. Under the operating conditions of the furnace, Zn volatilizes. The fumes are sent to bubble through a cooled Zn bath acting as condenser. The feed should not contain less than 40% of Zn. The amount of EAF dusts which can be processed in this process is limited by the large amounts of impurities they contribute.

[0021] Finally, Michigan Technological University tried to add to cupola furnace pellets of oxidized residues together
with cast iron and scrap. By operating at 1510-1538°C, a slag is formed and iron is reduced and recovered in the liquid state, whilst Zn and Pb are volatilized and recovered as raw zinc oxide. It should be considered that pelletized oxides only represent 5% of the charge fed to cupola furnace.

The facilities for performing the cited process require high investment costs and the resulting financial burdens are such that they can exclusively be supported by primary steelworks or consortia.

Only some from the above processes produce slags suitable for being disposed of to normal dumps.

EP-A-0 174 641 (Sumitomo) discloses a process for recovering valuable metals such as zinc, iron and the like from an iron dust containing zinc therein such as the one generated in an electric arc furnace for steel manufacture or the like.

The facilities for performing the cited process require high investment costs and the resulting financial burdens are such that they can exclusively be supported by primary steelworks or consortia.

The produced metals must be reprocessed in order to exploit them at commercial level.

The purposes of the present invention are of supplying a simple and direct process for:

- recovering, in metal form, iron contained in EAF dust;
- separating and concentrating, without losses, Zn and Pb oxides and other either metal or non-metal impurities (Cd, F, Cl, and so forth);
- removing all other components of dust, sending them to form a slag suitable for being disposed of to normal dumps, i.e., with no toxic or noxious character.

According to the present invention, in order to achieve the above purposes, a facility should be used which is suitable for small-medium production rates and possibly known by those skilled in steel making industry.

The energy and operating costs should be limited and anyway competitive with those of presently used processes for EAF dusts processing.

In order to achieve such purposes, the present invention proposes a process as claimed in claim 1.

The present invention is characterized, first of all, by the means selected to carry out the necessary reduction/oxidation reaction for rationally processing EAF dusts and oxidized zinc-bearing, high-iron materials, which are strongly penalized if the classic zinc production processes must be followed.

The low-frequency induction furnace of coreless type, which was selected according to the present invention, has been known for many years in secondary steel and non-ferrous metals metallurgy as a fast and effective smelting means.

According to the known art, such a furnace is only used as smelting means in which the charge in all known cases is constituted by cakes or scrap supplying high metal yields, variable according to the metal or alloy to be smelted.

For example, in the case of cast iron production, a charge which can be regarded as being standard, is as follows:

Clean cast iron cakes or scrap 95%
Master alloys 2-3%
Slagging agents 1-2%

According to the prior art, the low-frequency induction furnace is only used as smelting means for preparing liquid metal for casting.

On the contrary, the present invention uses, for the first time, the low-frequency induction furnace not as a melting means, but as an apparatus for carrying out simultaneously reduction and oxidation reactions and it therefore proposes of charging, for example, dust pellets typically having the following composition:

ZnO 16-24%
Fe₂ZnO₄ 10-12%
FeO 18-20%
MnO 2-4%
PbO 4-6%
CaO 6-8%
SiO₂ 4-5%
S 0.5-1%
F 0.5-1%
Cl 0.5-2%

wherein all metals are in their oxidized forms.

This surprising application according to the present invention is made possible by the characterizing feature
that the furnace, before starting charging the dust pellets, is filled up to approximately half height typically with cast iron, which constitutes the "heel" for the reaction. The high intensity flow of induced currents heats the bath up to 1450-1500°C and keeps it vigorously stirred. Now, the pellets, preferably dry and pre-heated, are charged to the furnace mixed with 14% of granular coal, with small amounts of slagging agents added.

**[0037]**  The reduction of the oxidized compounds to metal Zn takes place in the contact region between the surface of the cast iron bath and the lowermost, hottest layer of charged pellets. The continuous and fast renewal of cast iron layer which wets the ZnO and FeZnO₂ containing pellets, causes the reaction with carbon contained in cast iron:

\[
\text{ZnO} + C_{(\text{Fe})} \rightarrow \text{Zn} + \text{CO} \quad (1)
\]

to proceed with a considerably high rate.

**[0038]**  In its turn, the bath, owing to its contact with coal granules contained in the dust, restores the original C level of cast iron. Zn produced by reaction (1), owing to the high temperature of the reaction zone, vapourizes and rises through the layers of oxides of dust, effectively reducing iron oxides:

\[
\text{FeO} + \text{Zn} \rightarrow \text{Fe} + \text{ZnO} \quad (2).
\]

**[0039]**  The process takes place in two steps and in two different furnace zones:

-  a reductive step, in which the active agent is coal contained in cast iron, kept rapidly moving by the inductive phenomenon (steering). The interested zone is the bath/pellets contact region, which is the hottest region in the furnace and a large amount of energy must be supplied;
-  an oxidative step, which takes place inside the dusts, in which blended coal burns producing CO and generating the necessary energy to keep the high temperature value and allow iron oxides to oxidize Zn vapours rising from bottom.

**[0040]**  During the course of the process, the quality of formed slag must be carefully monitored, and, if so necessary, possibly modifying it with a suitable flux for fluidify it. Also the volatilization of Pb must be suitably assisted, by adding small amounts of CaCl₂ in order to cause low-boiling PbCl₂ to be formed by the reaction of added calcium chloride with PbO.

**[0041]**  A further object of the present invention is a facility for implementing the above disclosed process, which facility comprises an induction furnace for such a use as provided by the process according to the same invention.

**[0042]**  A facility according to the present invention is schematically disclosed by referring to the figure of the accompanying drawing.

**[0043]**  According to such figure, with (10) a low-frequency induction furnace of coreless type is shown, inside which, with (11), a charge of molten cast iron is schematically shown and, as one will see, only partially fills said furnace. Such charge is consequently present as a molten bath under turbulent conditions inside the furnace owing to the effect of the high intensity induced currents typical of induction furnaces.

**[0044]**  The dusts from electrical steelworks, rich in zinc and iron oxides, are fed to furnace (10) through the inlet (12), and they are thus obliged to flow along an inclined drum (13), in countercurrent relatively to the flow of hot air leaving from the furnace (10). The reaction heat generated inside the furnace is thus used to dry and pre-heat the dusts while they are flowing towards said furnace.

**[0045]**  The oxides of non-ferrous metals leave the furnace entrained by the stream of hot air rich in CO. The reaction of CO with the hood air:

\[
\text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2 \quad (3)
\]

takes place during the passage of said fumes through said inclined drum (13), along which the moist dust pellets flow downwards, countercurrently relatively to said fumes.

**[0046]**  Upon leaving the drum (13), the exhaust gases undergo a first cooling by the addition of air in (14) and enter a cyclone (15) in which the coarsest and heaviest components are removed. The complete dust removal takes place inside a sock or bag filter (16) of "pulse-Jet" type, installed upstream from a chimney (17).

**[0047]**  Non-limitative examples of a process according to the present invention are reported now.

**Example 1**

**[0048]**  By processing an EAF dust with normal composition (for example: a dust like the one described in following Example 2) according to the present invention, the following are obtained:
Inside a low-frequency induction furnace of coreless type having a capacity of 900 t/h of pelletized EAF dust can be processed, with the following consumptions:

<table>
<thead>
<tr>
<th>Material</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrical power</td>
<td>1000 kW/h</td>
</tr>
<tr>
<td>Coal</td>
<td>130 kg</td>
</tr>
<tr>
<td>CaCl₂</td>
<td>4 kg</td>
</tr>
<tr>
<td>CaF₂</td>
<td>4 kg</td>
</tr>
<tr>
<td>O₂</td>
<td>130 m³</td>
</tr>
<tr>
<td>CH₄</td>
<td>20 Nm³</td>
</tr>
<tr>
<td>Refractory material</td>
<td>6 kg</td>
</tr>
</tbody>
</table>

The above consumptions include all subsidiary operations (fume filtration, granulation air, and so forth).

Example 2

To a low-frequency furnace of coreless type with a power of 150 kW and with a capacity of 750 kg of cast iron, with refractory lining of alumina magnesite, 350 kg of cast iron was charged to be the reaction heel. The bath was heated up to 1450-1500°C and then the dust feed was started, consisting of 150 kg of dried and pre-heated pellets, and 20 kg of coal granules. The average composition of pelletized powders was:

- Zn 21.5%
- Pb 5.6%
- Fe 27.4%
- Mn 0.8%
- C 2.85%
- Ca 3.30%
- S 0.45%

In order to fluidify the slag, 0.1 kg of CaCl₂ and 0.3 kg of CaF₂ were gradually added throughout the test duration.

Within one hour after the test beginning, the addition of the charge had been completed and the reaction had proceeded to its end, with a fluid slag of acidic type and with a glassy appearance being formed.

The complete analysis of the slag was as follows:

- MgO 1.66%
- CaO 14.43%
- ZnO 1.98%
- FeO 12.27%
- PbO 0.05%
- Al₂O₃ 7.74%
- balance SiO₂

According to the release test, this slag meets the quality requirements of "A" Table.

From processing 150 kg of dusts, the following products were obtained:

- 38.5 kg of cast iron with 0.92% Mn, 3.6% C
- 52.5 kg of oxides with 58.3% Zn, 15.3% Pb, 0.44% Fe
- 53.0 kg of slag with 1.59% Zn, 0.05% Pb, 9.54% Fe

Summing-up, the following aspects of the invention are worth being highlighted:

1) The choice of the induction furnace which, while is very well-known as a smelting furnace, is used herein for carrying out reduction/oxidation reactions.
2) The intense agitation induced in the cast iron bath, so that the reduction of ZnO by alloyed carbon ZnO + C(Fe) → Zn + CO is favoured by the continuous renewal of the surface, caused by the intense induced currents flowing through the bath.
3) The reduction of FeO by Zn vapours evolving from the preceding reaction zone, multiplies the FeO reducing effect of coal contained in the charge.
4) The maximal energy exploitation of the available elements reduces the process consumptions.

Claims

1. A process for processing the electric steelworks dusts containing oxidised high-iron, zinc bearing materials mainly
in order to recover iron and zinc from them, comprising feeding said dusts in pellet form, coal and CaCl$_2$ or CaF$_2$ to a low-frequency induction furnace of coreless type (10), said process being characterized in that said low-frequency induction furnace of coreless type (10) is only partially filled with a charge (11) of cast iron, such a charge being contained inside said low-frequency induction furnace of coreless type (10) in the molten state as a bath under turbulent conditions owing to the effect of the induced currents, said dusts in pellets form coming into contact with the free surface of said turbulent molten bath inside said low-frequency induction furnace of coreless type (10), such that the continuous and fast renewal of cast iron layer wets the pellets, and the zinc oxide contained in the pellets reacts with carbon contained in said cast iron (11) of the bath/pellet contact region of said furnace (10) according to the following reaction (L):

$$\text{ZnO} + \text{C(Fe)} \rightarrow \text{Zn} + \text{CO} \quad (1)$$

and the metal Zn produced in the reaction (1) vaporises and reacts inside said low frequency induction furnace (10) with iron oxide contained in said dusts according to the following reaction (2):

$$\text{FeO} + \text{Zn} \rightarrow \text{Fe} + \text{ZnO} \quad (2)$$

and with oxygen injected by means of a lance inside said low-induction furnace (10), such that the heat generated results in the save of electrical energy.

2. Process according to claim 1, wherein said dusts are mixed with coal before feeding the low-frequency furnace.

3. Process according to claims 1 or 2, characterized in that the bath of molten cast iron keeps constant its carbon level by being into contact with said coal mixed with dusts.

4. Process according to anyone of claims 1-3, characterized in that said furnace is filled up to half height with cast iron before to start charging the dusts in pellet form.

5. Process according to any one of claims 1-4, characterized in that said dusts are fed to said furnace after being dried and pre-heated.

6. Process according to any one of claims 1-5, characterized in that said iron and zinc are prevailingly recovered as cast iron zinc oxide, respectively.

7. Process according to any one of claims 1-6, wherein the molten bath is heated up to a temperature of 1450 to 1500°C by the high intensity flow of induced currents.

Patentansprüche

1. Verfahren zur Verarbeitung des in elektrischen Stahlwerken anfallenden Abfallstaubs mit einem hohen Gehalt an Eisenoxiden und zinkhaltigen Stoffen vor allem zur Rückgewinnung von Eisen und Zink, umfassend die Einführung von Abfallstaub in Pelletform sowie Kohle und CaCl$_2$ oder CaF$_2$ in einen Niederfrequenzinduktionstiegelofen (10), dadurch gekennzeichnet, dass der Niederfrequenzinduktionstiegelofen (10) nur zum Teil mit einer Charge Gusseisen (11) beschickt wird, welche im Niederfrequenzinduktionstiegelofen (10) im flüssigen Zustand infolge der Wirkung der Induktionsströme als turbulente Schmelze vorliegt, wobei der pelletisierte Abfallstaub im Niederfrequenzinduktionstiegelofen (10) mit der freien Oberfläche der turbulenten Schmelze in Berührung kommt, sodass die kontinuierliche und rasche Erneuerung der Gusseisenschicht zur Benetzung der Pellets führte, wobei im Bereich der Kontaktschicht zwischen der Schmelze und den Pellets im Ofen (10) das in den Pellets enthaltene Zinkoxid mit dem im Gusseisen (11) enthaltenen Kohlenstoff gemäß dem folgenden Reaktionsschema (1)

$$\text{ZnO} + \text{C(Fe)} \rightarrow \text{Zn} + \text{CO} \quad (1)$$

reagiert und das durch die Reaktion (1) gebildete metallische Zink verdampft und innerhalb des Niederfrequenzinduktionstiegelofens (10)
mit dem im Abfallstaub enthaltenen Eisenoxid gemäß dem folgenden Reaktionsschema (2)

\[
\text{FeO} + \text{Zn} \rightarrow \text{Fe} + \text{ZnO} \quad (2)
\]
sowie mit über ein Strahlrohr in den Niederfrequenzinduktionsofen eingeblasenem Sauerstoff reagiert, sodass die erzeugte Wärme zur Einsparung elektrischer Energie führt.

2. Verfahren gemäß Anspruch 1, durchge gekennzeichnet, dass der Abfallstaub vor der Einführung in den Niederfrequenzofen mit Kohle gemischt wird.


4. Verfahren gemäß einem der Ansprüche 1 bis 3, durchge gekennzeichnet, dass der Ofen vor der Einführung des Abfallstaubs in Pelletform bis zur halben Höhe mit Gusseisen gefüllt wird.

5. Verfahren gemäß einem der Ansprüche 1 bis 4, durchge gekennzeichnet, dass der Abfallstaub vor der Einführung in den Ofen getrocknet und vorgewärmt wird.


7. Verfahren gemäß einem der Ansprüche 1 bis 6, durchge gekennzeichnet, dass die Schmelze durch den hochintensiven Fluss von Induktionsströmen auf eine Temperatur von 1450 bis 1500°C erhitzt wird.

Revendications

1. Procédé pour traiter les poussières émanant d’aciéries électriques contenant des matériaux oxydés antifrictions à base de zinc à haute teneur en fer, principalement afin de récupérer le fer et le zinc de celles-ci, comprenant l’alimentation desdites poussières sous forme de boulettes, de charbon et CaCl₂ ou CaF₂ dans un four à induction à basse fréquence de type sans noyau (10), ledit procédé étant caractérisé en ce que ledit four à induction à basse fréquence de type sans noyau (10) est seulement partiellement rempli d’une charge (11) de fonte, une telle charge étant contenue à l’intérieur dudit four à induction à basse fréquence de type sans noyau (10) à l’état fondu sous la forme d’un bain dans des conditions de turbulence dues à l’effet des courants d’induction, lesdites poussières sous forme de boulettes entrant en contact avec la surface libre dudit bain de fusion turbulent à l’intérieur dudit four à induction à basse fréquence de type sans noyau (10), de telle sorte que le renouvellement continu et rapide de la couche de fonte mouille les boulettes, et l’oxyde de zinc contenu dans les boulettes réagisse avec le carbone contenu dans ladite fonte (11) de la région de contact du bain et des boulettes dudit four (10) selon la réaction (1) suivante :

\[
\text{ZnO} + \text{C}_{(\text{Fe})} \rightarrow \text{Zn} + \text{CO} \quad (1)
\]
et le métal Zn produit dans la réaction (1) se vaporise et réagit à l’intérieur dudit four à induction à basse fréquence (10) avec l’oxyde de fer contenu dans lesdites poussières selon la réaction (2) suivante :

\[
\text{FeO} + \text{Zn} \rightarrow \text{Fe} + \text{ZnO} \quad (2)
\]
et avec de l’oxygène injecté au moyen d’une lance à l’intérieur dudit four à induction à basse fréquence (10) de telle sorte que la chaleur produite entraîne une économie d’énergie électrique.

2. Procédé selon la revendication 1, dans lequel lesdites poussières sont mélangées au charbon avant d’être alimentées dans le four à basse fréquence.

3. Procédé selon la revendication 1 ou 2, caractérisé en ce que le bain de fonte maintient sa teneur en carbone constante par le fait d’être en contact avec ledit charbon mélangé aux poussières.
4. Procédé selon l'une quelconque des revendications 1 à 3, caractérisé en ce que ledit four est rempli jusqu'à mi-hauteur de fonte avant de commencer le chargement des poussières sous forme de boulettes.

5. Procédé selon l'une quelconque des revendications 1 à 4, caractérisé en ce que lesdites poussières sont alimentées dans ledit four après avoir été séchées et préchauffées.

6. Procédé selon l'une quelconque des revendications 1 à 5, caractérisé en ce que ledit fer et ledit zinc sont récupérés principalement sous la forme de fer de fonte et d'oxyde de zinc, respectivement.

7. Procédé selon l'une quelconque des revendications 1 à 6, dans lequel ledit bain de fusion est chauffé jusqu'à une température de 1450 à 1500 °C par le flux de haute intensité des courants d'induction.