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Process for the heat treatment of metallic residues contaminated by organic compounds, and device for its implementation

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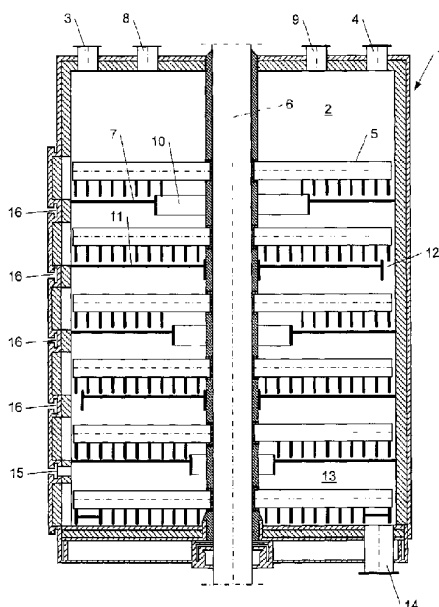
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(54) Title: PROCESS FOR THE HEAT TREATMENT OF METALLIC RESIDUES CONTAMINATED BY ORGANIC COM-
POUNDS, AND DEVICE FOR ITS IMPLEMENTATION

(54) Titre : PROCÉDE DE TRAITEMENT THERMIQUE DE RESIDUS METALLIQUES CONTAMINÉS PAR DES COM-
POSÉS ORGANIQUES ET DISPOSITIF POUR SA MISE EN ŒUVRE



(57) Abstract: Process and device for the treatment of divided metallic residues contaminated by one or more organic compounds, comprising: a mixing, inside a vessel, of said metallic residues with at least one calcium-magnesium compound capable of reacting exothermically with water; an exothermic reaction of said at least one calcium-magnesium compound by the water that the metallic residues contain; a temperature rise of the metallic residues undergoing an exothermic reaction; a dehydration of said metallic residues during this exothermic reaction; an oxidation of the organic compounds during said mixing, by bringing the metallic residues contaminated by one or more organic compounds mixed with said at least one calcium-magnesium compound into contact with a gas stream at least partly containing oxygen; and discharge, out of the vessel, of a dehydrated and handleable treated product that has a residual content of organic compounds of less than 1% by weight of said treated product.

(57) Abrégé : Procédé et dispositif de traitement de résidus métalliques divisés, contaminés par un ou des composés organiques, comprenant un brassage à l'intérieur d'une enceinte desdits résidus métalliques avec au moins un composé calco-magnésien capable de réagir avec de l'eau de manière exothermique, une réaction exothermique dudit au moins un composé calco-magnésien avec l'eau que les résidus métalliques contiennent, une

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élévation de température des résidus métalliques subissant une réaction exothermique, et une déshydratation desdits résidus métalliques pendant cette réaction exothermique, une oxydation des composés organiques au cours dudit brassage, par mise en contact des résidus métalliques contaminés par un ou des composés organiques mélangés audit au moins un composé calco-magnésien avec un courant gazeux contenant au moins partiellement de l'oxygène, et une évacuation hors de l'enceinte d'un produit traité déshydraté, manipulable, qui présente une teneur résiduelle en composés organiques inférieure à 1 % en poids dudit produit traité.

**PROCESS FOR THE TREATMENT OF CONTAMINATED METAL RESIDUES
AND APPARATUS FOR IMPLEMENTING IT**

The present invention relates to a process for the treatment and utilization of divided metal residues contaminated by one or more organic compounds, particularly hydrocarbons. The invention also relates to the apparatus for implementing the process.

The expression "divided metal residues" is understood to mean a collection of solid dust, chips, lamellae, flakes and/or granules or the like, of a metallic nature. These metal residues are mainly in the form of elementary metal compounds and/or metal oxides, but they may also appear in particular in sulphur-containing or chlorinated forms or as a mixture of the aforementioned forms. These divided metal residues are generally by-products of the iron-and-steel industry or non-ferrous metals. One of the families of these divided metal residues consists of hot-rolling oxides, often referred to by the term "mill scale". Another family comprises grindings and/or turnings resulting from the machining of metal parts.

These divided metal residues generally possess a high weight content of metal, greater than 30%, frequently greater than 50% or even 70% which it is desirable to utilize, in particular in the industry that has generated them.

These divided metal residues are very frequently contaminated by one or more organic compounds, particularly hydrocarbons, the latter possibly representing up to about 20% of the total mass. They are therefore sometimes denoted by the term "fatty scale" and usually contain a variable amount of water, which may be more than 20% of the total mass, hence their destructured nature - rolling mill scale constitutes one particular case thereof.

The presence of organic compounds often makes it necessary to pre-treat these by-products before recycling them, especially for environmental

reasons, it being possible for some of these organic compounds to be precursors of toxic compounds, such as volatile organic compounds (VOCs) and organochlorinated compounds, the most toxic ones of which are polychlorinated biphenyls (PCBs) dioxins and furans.

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Direct recycling of these divided metal residues also poses another problem: because of the presence of organic compounds and water, the by-product cannot easily be handled - it is inhomogeneous, sticky and unstructured. This is particularly the case when it is attempted to recycle mill scale from the steel industry into the process for sintering ore for feeding blast furnaces. In this case, apart from the handling difficulty, hydrocarbon vapours are given off and these foul the gas circulation system, in particular the fans and filters. Moreover, the aforementioned organic compounds may be converted during recycling to toxic compounds - specific decontamination of the gases must be provided.

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To meet the regulations relating to the discharging of the aforementioned toxic compounds, industrial practice shows that it is necessary to greatly limit the content of organic compounds in mill scale or other divided metal residues, during their recycling, owing to the limitations of methods for decontaminating the gases, especially as regards the filters.

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It is known to treat oily mill scale by intimately mixing it with calcium oxide, mainly in the form of quick lime. In chapter 38 of a work on a recent review of the prior art in this field, the author (F. Bölsing, "Dispersing by Chemical Reactions Remediation Technology", in D. Wise *et al.*, "Remediation engineering of contaminated soils", by Marcel Dekker Inc., 2000) proposes a treatment in two steps:

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- addition of quick lime to the medium contaminated by hydrocarbons, especially steel mill scale (predistribution step); and
- intensive mixing, possibly in a grinder, so as to produce a homogeneous dispersed medium and to allow oil to be transferred to the lime;

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quick lime CaO also picks up all or some of the water present in the mill scale, converting it to slaked lime Ca(OH)₂ (dispersion step).

5 The lime combined with the oil can then be easily separated from the iron and iron oxide particles, by screening. Magnetic separation may also allow the finest metal particles to be recovered.

10 The author also points out that it is often necessary to pre-treat the quick lime by means of an additive that slows down the reaction of slaking the lime with the water from the mill scale, otherwise this very rapid slaking reaction takes place before the oil can be absorbed by the lime.

15 A more recent patent application (US 2005/0256359) indicates the possibility of using lime to reduce the toxicity of organic compounds, in particular by eliminating the halogens of toxic compounds, of the dioxin, furan or polychlorinated biphenyl type. Apart from its aforementioned role, lime acts as nucleophilic reactant, promoting the substitution of halogens with hydroxyl groups followed by oxidative degradation of the substituted molecules, in order to give organic molecules that are non-toxic or of low toxicity. Non-toxic organic
20 compounds are preferably added so as to promote auto-ignition of the dispersed medium. In that document, only the "dehalogenation" yields - the intended objective - are specified, but not the possible levels of reduction of the organic substances.

25 Also known is a process for the treatment of divided metal residues contaminated by one or more organic compounds, in particular one or more hydrocarbons, comprising:

- mixing, inside a chamber, of said metal residues with at least one calcium/magnesium compound capable of reacting exothermically with water;
- 30 - exothermic reaction of said at least one calcium/magnesium compound with the water that the metal residues contain;

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added so as to promote auto-ignition of the dispersed medium. In that document, only the "dehalogenation" yields - the intended objective - are specified, but not the possible levels of reduction of the organic substances.

5 Also known is a process for the treatment of divided metal residues contaminated by one or more organic compounds, in particular one or more hydrocarbons, comprising:

- mixing, inside a chamber, of said metal residues with at least one calcium/magnesium compound capable of reacting exothermically with water;

10 - exothermic reaction of said at least one calcium/magnesium compound with the water that the metal residues contain;

- rise in temperature of the metal residues subject to an exothermic reaction; and

- dehydration of said metal residues during this exothermic reaction.

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This process is described in Japanese Patent Application JP2000-237512. In particular, it proposes a method of dehydrating iron and steel residues intended to be reused as pig iron dephosphorizing agent. The product resulting from this treatment is considered to be handleable. One application case teaches that the addition of 20% quick lime by weight to the residues makes it possible to reduce the free oil content from 2.9% initially to 1.9% after treatment, the difference being absorbed by the lime. The authors propose using these treated residues containing partly absorbed oil as auxiliary material in steelmaking, where the oil will be burnt off, according to the authors, without a negative effect on the cast steel.

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The patent EP1645645 describes a thermal treatment of steel plant sludges in a multi-stage furnace and the treated sludges at the exit of the furnace have a temperature between 700 °C and 800 °C.

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Finally, patent US 4 326 883 describes a process for de-oiling and agglomerating mill scale. It consists of two steps:

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COMBUSTION: in this next step, the pellets are heated in an oxidizing atmosphere to a temperature sufficient to cause ignition and almost complete combustion of the oil contained in the pellets. The pellets advance as a moving bed from 2.5 to 7.5 cm in thickness so as to reside for from 0.5 minutes to 2 minutes in an atmosphere at between 815°C and 1100°C, taking measures to ensure that the pellets do not exceed a temperature of 345°C. The importance of the above preparations step is reflected in the possibility of almost completely eliminating, in a very short time, the oil present on the surface of the pellets. This technique makes it possible to use the calorific value of the oil, so as to reduce the consumption of external fuel, which nevertheless remains substantial.

However, patent US 4 326 883 is limited in its description and its examples to mill scale containing no more than 1% oil. This is because it is probably difficult, with higher oil contents, to produce pellets for which the oil will mainly be present as a surface layer, so as to allow flash combustion of the pellets in less than 2 minutes.

To remedy the drawbacks of the aforementioned prior art, the object of the present invention is to provide a process and a device for the treatment of divided metal residues contaminated by organic compounds, which are simple and suitable for a wide range of contents of organic compounds and make it possible to limit to the strict minimum the supply of energy via external fuels, while still delivering a particularly valuable product that can be utilized.

To solve these problems, the invention provides a process that comprises the steps:

- mixing, inside a chamber, of said metal residues with at least one calcium/magnesium compound capable of reacting exothermically with water;
- exothermic reaction of said at least one calcium/magnesium compound with the water that the metal residues contain;

- rise in temperature of the metal residues subject to an exothermic reaction;
 - dehydration of said metal residues during this exothermic reaction;
 - oxidation of the organic compounds during said mixing, by bringing
- 5 the metal residues contaminated by one or more organic compounds mixed with said at least one calcium/magnesium compound into contact with a gas stream containing at least partly oxygen; and
- removal from the chamber of a handleable and directly useable
- 10 dehydrated treated product having a residual content of organic compounds of less than 1% by weight of said treated product.

The process is controlled so as to keep the treatment temperature, notably that of the gas stream, during the different steps below 600°C.

15 According to the invention, a calcium/magnesium compound is therefore added to the contaminated, divided metal residues in a chamber suitable for the heat treatments, which is swept with a gas stream and in which the entire treatment is carried out, and therefore preferably in a single step. No prior preparation or preconditioning of the materials to be treated, either of the calcium/magnesium compound or of the mixture thereof, is necessary. As in

20 practice the residues often contain sufficient water, the process according to the invention does not in principle require any addition of water or even of additional reactants. The product leaving said chamber is dehydrated, easily handleable, directly useable or recyclable, e.g. in a metallurgical or steelmaking process, and has a very low content of organic compounds. This product can then be

25 utilized directly, especially in the industry from which the recovered metal originated.

The invention therefore proposes mainly a substantially autothermal process for eliminating organic compounds, particularly hydrocarbons, from

30 contaminated metal residues, by means of a calcium/magnesium compound.

According to the invention, said at least one calcium/magnesium compound satisfies formula I:



in which x is a molar fraction greater than 0 and equal to or less than 1.

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This compound is preferably in the form of solid particles, mainly in oxide form. This calcium/magnesium compound may contain impurities, such as silica, alumina, iron oxide and calcium carbonate in an amount of a few per cent, and hydroxides corresponding to the oxides of the formula I.

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One particular case of a calcium/magnesium compound is quick lime, corresponding to the case in which x is equal to 1 in formula I, which may also contain the aforementioned impurities and also a small amount of magnesium oxide.

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Although it is possible in principle to start the oxidation reaction solely by the energy provided by the exothermic reaction between quick lime and water, it may be advantageous to furthermore supply the initial activation energy. According to one advantageous method of implementing the invention, the process therefore furthermore comprises:

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- an initial supply of heat in order to promote onset of said exothermic reaction of the organic compounds contained in the metallic residues and to reach a predetermined temperature of the contaminated metal residues; and
- this supply is cut off when said predetermined temperature is reached, the process then being substantially autothermal in the steady state.

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In the process according to the invention, a minimum amount of heat may be provided by any type of heating known per se, *a priori* most particularly or only in the onset phase. The predetermined temperature reached is then maintained essentially or completely by exothermic reactions that take place in the chamber.

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The term "autothermal" means, within the context of the present invention, that the process no longer requires in principle a supply of external energy, it being possible for the reactions to be entirely controlled by adjusting the gas stream containing at least partly oxygen, the supply of metallic residues and the supply of calcium/magnesium compound.

Preferably, the residual content of organic compounds of the treated product is less than 0.5% by weight, advantageously less than 0.2% by weight and in particular less than 0.1% by weight.

During the treatment, the treatment of the metal residues advantageously takes place at a temperature of $\geq 200^{\circ}\text{C}$ to $\leq 600^{\circ}\text{C}$. Typically, the various conversions are carried out at temperatures from 300°C to 550°C , thereby allowing the use of light solutions for protecting the walls of the treatment chamber, without requiring the use of refractory bricks. Apart from the inlets for the aforementioned materials, the chamber must allow the entry of fresh oxygen-containing gas, especially air, and the outlet for the hot gases, wherein the injection of fresh air may also be used to control the treatment temperature. A means of homogenizing the introduced materials ensures that the solid charge, consisting of said contaminated metal residues and said at least one calcium/magnesium compound, is continuously stirred and aerated. This charge may remain for about 0.25 h to 5 h, preferably 0.5 h to 2 h, in the treatment chamber so as to obtain the treated product.

The contaminated residues may preferably contain up to about 20% by weight, e.g. up to 15% by weight, of organic compounds and more than 20% by weight of water, for example up to 30% by weight. In general, they contain from 2% to 6% of organic compounds and 10% to 15% by weight of water.

The treated product is dehydrated and is in a powdery and easily handleable form and may even be able to be granulated by simply adding water.

The amount of calcium/magnesium compound added to the contaminated metal residues depends mainly on the amount of organic compounds, but also on the amount of water initially present in these residues.

5 In general, the calcium/magnesium compound represents 5% to 35%, preferably 8% to 20%, often around 10% of the total mass of the aforementioned solid charge.

10 According to one particular method of implementing the invention, the process comprises a movement of said solid charge in the chamber during the mixing with supply of the gas stream countercurrently with the solid charge. The process advantageously includes, while the residues are being mixed and brought into contact with a gas stream, almost complete oxidation of the organic compounds, which are essentially converted to water and CO₂.

15 According to an improved method of implementing the invention, the process comprises recycling said treated product, preferably directly, into a metallurgical or steelmaking process, said treated product being substantially formed from possibly partly oxidized metal compounds and from said at least
20 one hydrated and possibly also carbonated calcium/magnesium compound. The almost complete absence of residual organic compounds means that the product treated according to the invention can be recycled directly. In particular in the case of mill scale, this could be directly recycled into the ore sintering process carried out before the blast furnace. The presence of the
25 calcium/magnesium compound is also beneficial in the aforementioned sintering process.

30 Other features of the process according to the invention are indicated in the appended claims.

The present invention also relates to an apparatus for the treatment of divided metal residues contaminated by organic compounds. This apparatus comprises a chamber, advantageously a heat-resistant chamber, which has:

- 5 - at least one solids inlet via which said contaminated residues and at least one calcium/magnesium compound capable of exothermically reacting with water are introduced into the chamber;
- at least one mixing element which mixes said contaminated residues and said at least one calcium/magnesium compound; and
- 10 - at least one solids outlet, via which a handleable, dehydrated, treated product is removed, which is directly useable or recyclable e.g. in a metallurgical or steelmaking process.

According to the invention, the chamber of this apparatus furthermore has:

- 15 - at least one gas inlet for introducing a gas stream containing at least partly oxygen into the chamber; and
- at least one gas outlet,
- said treated product removed at said at least one solids outlet having a residual content of organic compound of less than 1% by weight of said
- 20 treated product.

As already indicated above, an important advantage of such a device is the fact that it does not comprise refractory bricks.

- According to one advantageous embodiment of the apparatus according to the invention, said at least one solids inlet is located at one end of the chamber and said at least one solids outlet is located at the opposite end of the chamber, the abovementioned metal residues mixed with said at least one calcium/magnesium compound being moved between said at least one inlet for solids and said at least one outlet for solids, and said at least one gas inlet and
- 25
 - 30
- said at least one gas outlet are arranged in the chamber so that said gas stream passes countercurrently with the abovementioned mixed residues.

Advantageously, such an apparatus allows a continuous process to be carried out in one step. It would be possible for example to make use of a vertical multi-zone (multi-stage) chamber or a horizontal chamber, with separate feeds for the contaminated residues and for the calcium/magnesium. In this case, the first zone (feed zone), for example the upper stage of the chamber in the vertical version, serves for collecting the two feeds of solids and for continuously mixing them by means of a homogenization device. The feed stage also serves for preheating the solid charge by the hot gases escaping therefrom. The other zones or stages, located lower down, provide a sufficient residence time, while still aerating the material and circulating the gas flow, preferably countercurrently with the solids. It is thus possible to control the oxidation of the solids. The last zone or bottom stage, for outlet, is used in particular for preheating the gases by the solids and conversely cooling the latter by the fresh gas.

It is also possible to use a cylindrical chamber slightly inclined to the horizontal, with a gravity feed of the material, either by movement of the chamber with a stationary mixing device, or by movement of the mixing device in a stationary chamber, or by a combination of these two possibilities.

In such an apparatus according to the invention, the maximum temperature of the solid charge and of the gas stream does not exceed 600°C and is typically between 200°C and 550°C. The fresh gas, preferably flowing countercurrently, cools the solid charge before its exit from the chamber, while being heated upon contact with said charge. Similarly, the hot gases heat the solid charge in the stage where the two solids are fed and homogenized.

Surprisingly, it thus appears to be possible to carry out the treatment of contaminated residues into treated residues according to the invention with no or virtually no external heat supply, namely without the use of specific fuel, at least during steady-state operation. A supply of energy is possibly required only for an initial rise in temperature in the onset phase.

To achieve this result, it is necessary to make use of the heat generated by all of the exothermic reactions that take place during the treatment. This objective is achieved according to the invention in which the treatment process is carried out in a single step, in a single chamber.

The various exothermic reactions that take place in the treatment chamber are:

- the slaking or hydration of the calcium/magnesium compound with the water present in the contaminated residues, namely the conversion of calcium oxide and/or magnesium oxide to the corresponding hydroxide;
- the almost complete oxidation of most of the organic compounds, which are essentially converted to water and CO₂;
- the carbonation of the calcium/magnesium compound; and
- possibly the at least partial oxidation of the metal compounds/contaminated residues into corresponding metal oxides.

Surprisingly, it appears that by controlling the conditions, in terms of residence time, aeration of the material and temperature, it is possible for the oxidation of the metal compounds, associated with the release of heat from the other reactions, to make the process autothermal, at least in the steady state.

Other features of the apparatus according to the invention are indicated in the appended claims.

Other details and features of the invention will become apparent from the description given below by way of non-limiting example, with reference to the appended drawings.

Figure 1 shows a schematic sectional view of a treatment apparatus according to the invention.

Figure 2 shows a sectional view of one embodiment.

In the various figures, identical or similar elements are denoted by the same references.

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A preferred apparatus for carrying out the process according to the invention is shown in Figure 1 for the particular case of the treatment of steel mill scale.

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The equipment illustrated in Figure 1 consists of a multi-stage chamber 1 allowing treatment at temperatures ranging up to 600°C. This permits the use of a non-refractory technology, easy to carry out and inexpensive. This chamber is advantageously equipped with external burners (not shown) which supply heat, if necessary, namely if the temperature of the chamber drops below 300°C. The upper stage 2 (feed stage) is used for feeding the contaminated mill scale and the calcium/magnesium compound, preferably via two separate inlets 3 and 4. The feed stage 2 further includes a homogenizing means, preferably in the form of one or more rabble arms 5 rotating about a central shaft 6, mixing the solids that accumulate on the fixed hearth 7. It is also possible to provide one or more fixed rabble arms in the presence of a rotating hearth for the rabble arms and moving hearths, or a combination of these variants. In the example illustrated, two gas outlets 8 and 9 allow the ascending hot gases to be discharged, after heat exchange with the fed solids.

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These preheated solids drop, by passing through a central hole 10, onto the hearth 11 of the underlying stage. During this cascade, exchange takes place between the gas flow and the solids. The hearth 11 is provided with one or more peripheral orifices 12 via which the mixed solids pass, through at least one further rabble arm, to the underlying stage. Similarly, the solids are conveyed by successive steps as far as the last stage (output stage 13), while being mixed with maximum exchange between the solids and the gas flow, in particular so as to promote the aforementioned oxidation reactions.

The output stage 13 serves in particular to preheat the fresh gas and cool the treated mill scale. In particular it comprises an outlet 14 for discharging this treated mill scale and a gas inlet 15 for introducing an oxygen-containing gas.

The number of stages of the apparatus depends mainly on the residence time needed for the fullest oxidation of the organic compounds initially present. Heated or unheated air may optionally be introduced as a supplement at each stage via the gas inlets 16.

Figure 2 shows a single-stage chamber 17, which can be heated by electrical heating elements 22, of cylindrical shape and equipped with a rabble arm 18 rotating at about 3 rpm. It is provided with equipment for introducing the solids 19, with an air inlet 20 and a gas outlet 21, and also with a pipe 23 for measuring the temperature of the solids and for removing samples.

In all the examples given below, rolling mill scale is treated with quick lime of industrial quality. The initial hydrocarbon content of the contaminated mill scale, or the final content of the treated mill scale, is determined by tetrahydrofuran extraction in a Soxhlet extractor followed by "Rotavapor" distillation. The contaminated mill scale is dried beforehand at 105°C. When the measured hydrocarbon content is less than 0.1%, it is considered that the treated mill scale is free of residual hydrocarbons.

In all cases the mill scale is treated in a pilot plant, such as that shown in Figure 2, using a common operating method.

The operating conditions are the following:

- preheating of the furnace to the predetermined initial temperature;
- introduction of material, alternating between lime and mill scale;
- continuous stirring of the mixture;

- measurement of the temperature of the solids, so as to monitor the progress of the exothermic reactions;
- removal of a sample at the end of the trial;
- stopping of the reaction in the sample by contact with liquid nitrogen (oxygen-free cooling and atmosphere); and
- measurement of the residual hydrocarbon content of the sample removed.

Example 1

7.4 kg of mill scale containing 6% hydrocarbons by weight and 14% water by weight were treated in the pilot plant with 1.6 kg of lime, i.e. a lime supply of 18% by weight.

Two similar treatments were carried out by varying the initial treatment temperature; the first case at 200°C, the second at 300°C. In both cases, the treated product was pulverulent and easily handleable, and its residual hydrocarbon content was less than 0.1%.

At an initial temperature of 200°C, there was an induction period of about 1.5 h before significant release of heat by the oxidation reactions that make the operation autothermal. There was no external supply of heat after this moment. The maximum temperature of the solids was approximately 450°C. An overall residence time of about 3 h was needed to completely remove the hydrocarbons.

At 300°C the induction period did not exceed 0.5 h. The maximum temperature of the solids was higher, slightly above 500°C. The residence time needed to oxidize all the hydrocarbons was less than 2 h.

This example shows the usefulness of having an external supply of heat so as to significantly reduce the induction period and thereby the overall residence time for complete oxidation of the hydrocarbons.

Example 2

5 Mill scale contaminated with 1.7% hydrocarbons by weight and 14%
water by weight was treated at an initial temperature of 300°C. An addition of
quick lime of 18% by weight was used, i.e. 1.6 kg of lime per 7.5 kg of mill
scale. The treated product was pulverulent and easily handleable, and its
residual hydrocarbon content was less than 0.1%.

10 This experiment was compared with the second one of example 1,
carried out under similar conditions (300°C and 18% lime) but starting with mill
scale more contaminated with hydrocarbons (6%).

15 When the initial hydrocarbon content was lower, the maximum
temperature reached by the solids was lower, below 500°C, and this occurred
after a shorter residence time, of less than 1.5 h.

Example 3

20 The heat treatment of charges containing hydrocarbons generally results
in the substantial emission of VOCs (volatile organic compounds). It was
therefore useful to estimate the situation in the case of treatment according to
the invention.

25 10 kg of mill scale containing 2.9% hydrocarbons by weight and 19%
water by weight were treated at an initial temperature of 300°C in the pilot plant
of Figure 2 with 2.5 kg of quick lime, i.e. a 20% by weight supply of lime. The
treated product was pulverulent and easily handleable, and its residual
hydrocarbon content was less than 0.1%.

30 Under the conditions of this experiment, an average VOC content
of 1500 mg/Sm³ in the gas discharge was observed if the carbon of the mill
scale hydrocarbons was completely converted to VOCs. In fact, a VOC
measurement during the experiment showed however a much lower average

content of less than 60 mg/Sm³. Thanks to this process for treatment with lime, the VOC emission was therefore about 25 times lower on average.

5 It should be understood that the present invention is in no way limited to the methods of implementation described above and that many modifications may be made thereto without thereby departing from the scope of the appended claims.

Claims:

1. Process for the treatment of divided metal residues contaminated by one or more organic compounds, comprising:
- 5
- mixing, inside a chamber, of said metal residues with at least one calcium/magnesium compound capable of reacting exothermically with water;
 - exothermic reaction of said at least one calcium/magnesium compound with the water that the metal residues contain;
- 10
- rise in temperature of the metal residues subject to an exothermic reaction;
 - dehydration of said metal residues during this exothermic reaction;
 - oxidation of the organic compounds during said mixing, by bringing the metal residues contaminated by one or more organic compounds
- 15
- mixed with said at least one calcium/magnesium compound into contact with a gas stream containing at least partly oxygen; and
 - removal from the chamber of a handleable dehydrated treated product having a residual content of organic compounds of less than 1% by weight of said treated product,
- 20
- the process being controlled so as to keep the temperature of the gas stream below 600°C.
2. Process according to claim 1, characterized in that said at least one calcium/magnesium compound satisfies formula I:
- 25
- $$x\text{CaO} \cdot (1-x)\text{MgO} \quad (I)$$
- in which x is a molar fraction greater than 0 and equal to or less than 1.
3. Process according to either of claims 1 and 2, characterized in that it furthermore comprises:
- 30
- an initial supply of heat in order to promote onset of said exothermic reaction and to reach a predetermined temperature of the contaminated metal residues; and

- this supply is cut off when said predetermined temperature is reached, the process then being autothermal in the steady state.
- 5 4. Process according to any one of claims 1 to 3, characterized in that the residual content of organic compounds of the treated product is less than 0.5% by weight.
 - 10 5. Process according to any one of claims 1 to 4, characterized in that, during the mixing, the metal residues have a temperature of around 300°C to 550°C.
 - 15 6. Process according to any one of claims 1 to 5, characterized in that the temperature of the gas stream is controlled by injection of air.
 - 20 7. Process according to any one of claims 1 to 6, characterized in that the calcium/magnesium compound represents 5 to 35% of the total mass consisting of said metal residues and of the calcium/magnesium compound.
 - 25 8. Process according to any one of claims 1 to 7, characterized in that it comprises, during mixing, movement in the chamber of the metal residues mixed with said at least one calcium/magnesium compound with a supply of the abovementioned gas stream countercurrently with the metal residues.
 - 30 9. Process according to any one of claims 1 to 8, characterized in that the contaminated residues contain up to about 20% by weight of organic compounds and up to about 30% by weight of water.
 10. Process according to any one of claims 1 to 9, characterized in that, in the chamber, the metal residues are mixed with said at least one

calcium/magnesium compound and brought into contact with said gas stream for a residence time of 0.25 h to 5 h.

11. Process according to any one of claims 1 to 10, characterized in that it comprises recycling said treated product into a metallurgical or steelmaking process, said treated product being substantially formed from possibly partly oxidized metal compounds and from said at least one hydrated and possibly also carbonated calcium/magnesium compound.

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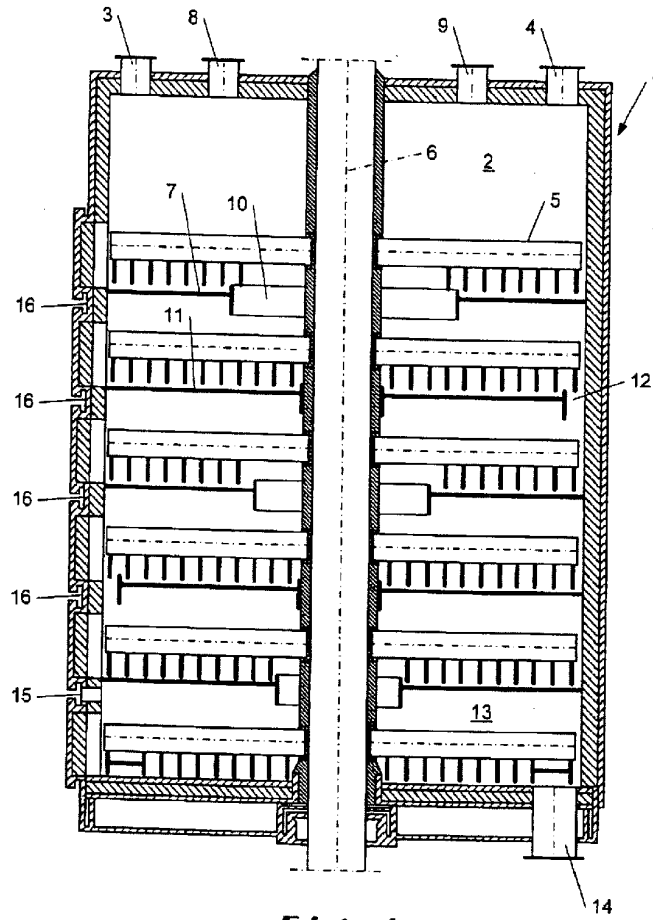


Fig. 1

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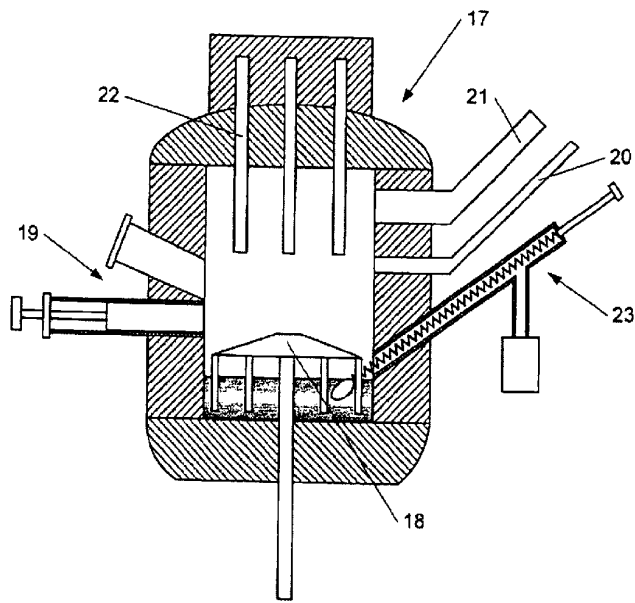


Fig. 2