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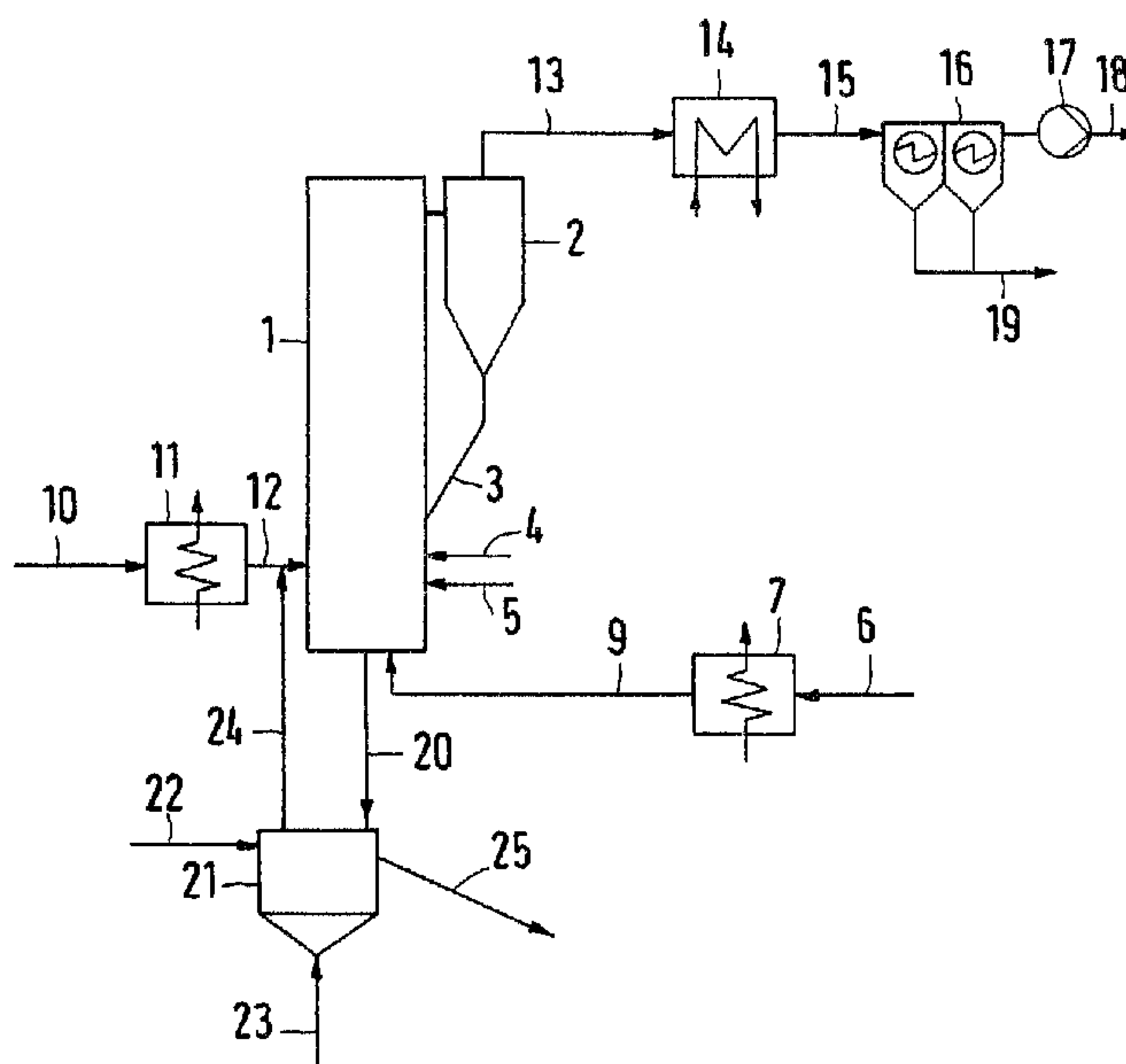
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(54) Titre : METHODE POUR TRAITER LES RESIDUS D'USINES METALLURGIQUES RENFERMANT DU ZINC ET DU PLOMB

(54) Title: METHOD OF REPROCESSING ZINC- AND LEAD-CONTAINING RESIDUES FROM METALLURGICAL PLANTS



(57) Abrégé/Abstract:

Zinc- and lead-containing residues from metallurgical plants are reprocessed by a thermal treatment in a circulating fluidized bed system. A major part of the heat demand is satisfied by a combustion of solid carbon in the fluidized bed reactor of the circulating fluidized bed system. A reducing fluidizing gas, which is virtually free of free oxygen, is fed to the lower part of the fluidized bed reactor. A solid carbon content from 5 to 30 % is adjusted in the fluidized bed in the lower portion of the fluidized bed reactor, which is supplied in its upper portion with oxygen-containing gases and in which CO₂ is formed only at such a rate that zinc metal is not reoxidized. Substantially all solids are removed in a recycling cyclone from the suspension which has been discharged and are recycled. The gas is cooled to a temperature at which zinc metal is oxidized to ZnO. The dustlike zinc compounds and lead compounds are removed from the gas,

ABSTRACT

Zinc- and lead-containing residues from metallurgical plants are reprocessed by a thermal treatment in a circulating fluidized bed system. A major part of the heat demand is satisfied by a combustion of solid carbon in the fluidized bed reactor of the circulating fluidized bed system. A reducing fluidizing gas, which is virtually free of free oxygen, is fed to the lower part of the fluidized bed reactor. A solid carbon content from 5 to 30 % is adjusted in the fluidized bed in the lower portion of the fluidized bed reactor, which is supplied in its upper portion with oxygen-containing gases and in which CO_2 is formed only at such a rate that zinc metal is not reoxidized. Substantially all solids are removed in a recycling cyclone from the suspension which has been discharged and are recycled. The gas is cooled to a temperature at which zinc metal is oxidized to ZnO . The dustlike zinc compounds and lead compounds are removed from the gas.

This invention relates to a method of reprocessing zinc- and lead-containing residues from metallurgical plants by a thermal treatment at elevated temperatures and under reducing conditions whereby zinc and lead are volatilized, higher iron oxides are reduced as fully as possible to FeO and zinc and lead vapor are removed from the exhaust gas after it has been cooled.

In the making of pig iron and steel, residues consisting of dusts and sludges are formed in various processing stages, e.g., in the sintering plants, at the blast furnace and in rolling mills. Said residues consist mainly of iron but contain small amounts of zinc, lead and alkalis and/or are contaminated with oil. They cannot readily be recycled to the processing, e.g., via

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the sintering plant, because their contents of zinc, lead and alkalies give rise to difficulties in the blast furnace process. The dumping of such residues becomes more and more difficult for ecological reasons and considerable amounts of iron, zinc and lead would be lost in a dump. For this reason the contents of zinc, lead, alcalis and oil in such residues must be decreased before they can be recycled to a sintering plant.

In known processes, zinc, lead and alkalies are volatilized under reducing conditions and a considerable part of the iron oxides is reduced to metallic iron. The sintering of the residues which have thus been pretreated results in a reoxidation of their iron metal content. Besides, the sintering process may be adversely affected by the iron metal contained in the mixture to be sintered.

In other known processes the iron content is reduced only to FeO.

German Patent Publication 10 56 157 discloses a process in which zinc-containing iron ores are treated in a fluidized bed whereby an exhaust gas is formed which contains zinc in part as zinc metal and in part as zinc oxide; the iron oxides are at least in part reduced to FeO. But for a faster dezincking the iron oxides must be reduced to iron metal. The zinc-containing iron ores are fed as pellets having a size

of the order of millimeters. The fluidized dust is collected from the exhaust gas in a hot cyclone and is recycled to the fluidized bed. The purified exhaust gas is afterburnt with oxidation of zinc metal to ZnO, which is then collected in dust collectors. The reducing gas is introduced from below through a tubular gas feed port. A discontinuous operation has been described because the dezincd material can be discharged through the tubular gas feed port when the supply of gas has been discontinued.

In French Patent Specification 2,373,612 and on pages 85 to 103 of "Proceedings Ist. Proc. Technol. Conference", Washington, it has been described that zinc and lead can be volatilized without a formation of iron metal if coal is not used as a reducing agent. For this reason the carbon is removed from dusts which have been formed in metallurgical plants and have a relatively high content of solid carbon before such dusts, which may consist, e.g., of blast furnace dust, are subjected to a reducing treatment. That removal of carbon may be effected by physical processes or the solid carbon content may be almost entirely combusted under oxidizing conditions in a preceding separate stage. The material is treated on traveling grates or in shaft furnaces. A separate process stage is required for the removal of solid carbon and part of the heat generated by the combustion of solid carbon is lost for the process.

It is an object of the invention to provide for the reprocessing of residues from metallurgical plants a continuous method which permits a reducing treatment in the presence of solid carbonaceous material in conjunction with an effective volatilization.

That object is accomplished in accordance with the invention which provides a method of reprocessing a zinc and lead containing residue from a metallurgical plant comprising:

10 introducing the residue into a fluidized bed reactor means of a circulating fluidized bed system comprising the reactor means, cyclone means and recycle means;

 thermally treating the residue at an elevated temperature and under reducing conditions in said reactor means;

 volatilizing zinc and lead;

 reducing higher iron oxides as fully as possible to FeO;

20 introducing a reducing fluidized gas virtually free of free oxygen into a lower portion of the fluidized bed reactor means;

 controlling the rate and composition of the fluidized gas to maintain in the lower portion of the reactor such a reduction potential that at least 80% of the iron content is present as Fe²⁺, not in excess of 1% iron content is present as metal iron and the balance being present as Fe³⁺;

30 introducing a solid carbonaceous material into the reactor means and adjusting the solid carbon content in the lower portion thereof to about 5 to 30%;

supplying an oxygen-containing gas to an upper portion of the reactor means;

supplying a portion of the heat demand for the thermal treatment from the combustion of the carbonaceous material and forming CO_2 at a rate insufficient to reoxidize zinc metal;

forming a gas-solids suspension in the reactor means and discharging the suspension at an upper portion thereof;

10 removing solids from said suspension in the cyclone means and recycling the removed solids to the reactor means at a rate per hour equivalent to at least 5 times the weight of the solids contained in the reactor means;

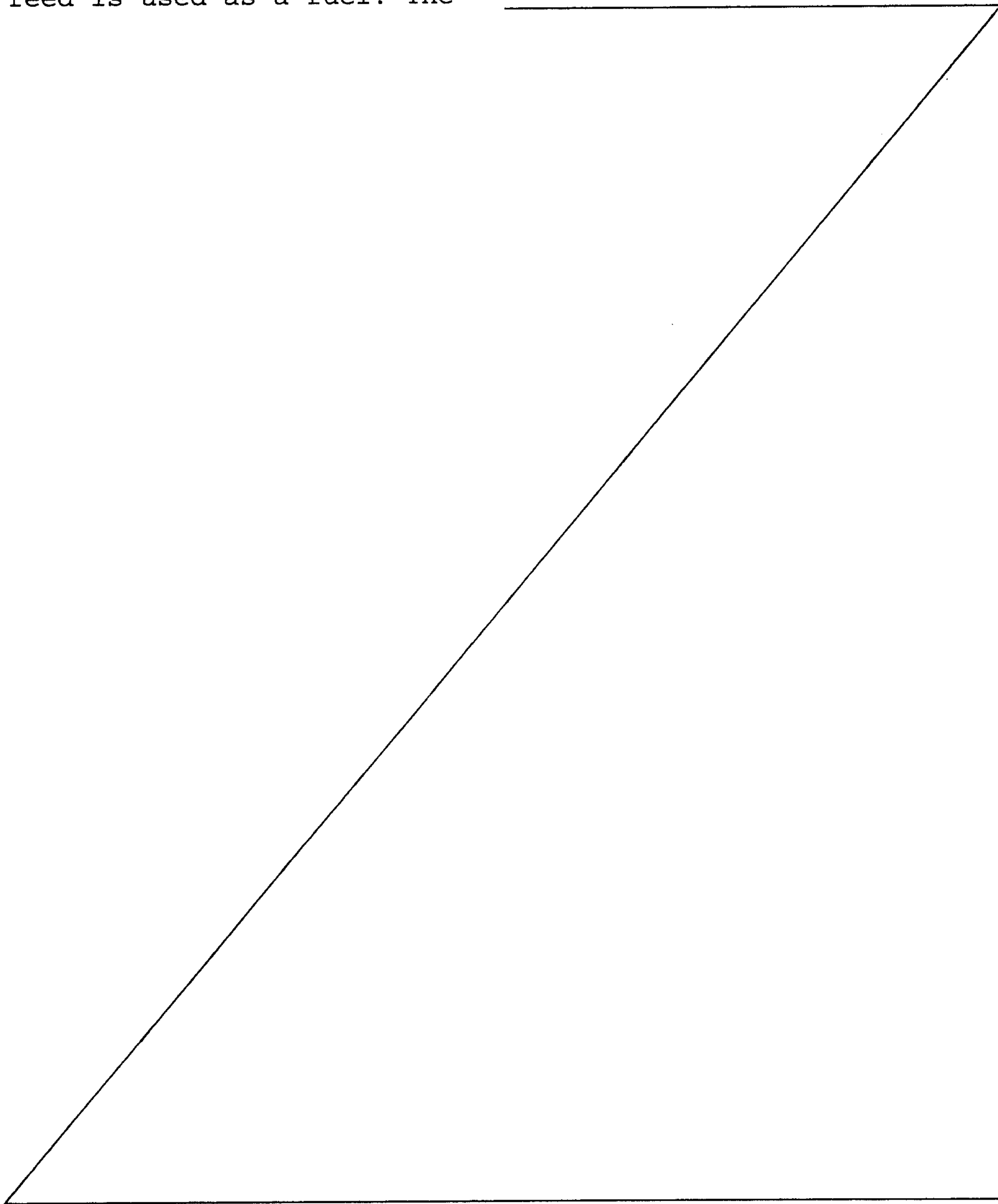
exhausting a cleaned gas from the cyclone means and cooling the gas to a temperature at which zinc metal is oxidized to ZnO ; and

removing a dust-like zinc compound and lead compound from the gas.

20 The residues from metallurgical plants may particularly consist of dust from blast furnace top gas, dust from steelmaking converters, and dust from electric furnaces, which dusts have been formed in the making of iron and steel. When residues formed in the electrolytic production of zinc are used, any jarosite residue must be subjected to a decomposition of sulfates before it is treated. The residues to be treated may have a particle size up to about 3 mm. The lower zone of the fluidized bed reactor is operated under more strongly reducing conditions
30 than the upper zone. The lower zone extends up to about 30% of the height of the fluidized bed reactor. A solid carbon

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metal which has entered the upper zone with the feed are oxidized to Fe^{2+} and the remainder to Fe^{3+} except for not in excess of 1% iron metal so that said iron metal in the feed is used as a fuel. The



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reducing fluidizing gas may particularly consist of coke oven gas^{or converter gas} formed in steelmaking processes. The oxygen-containing gas which is employed may consist of air, oxygen-enriched air and commercially pure oxygen. A temperature from 900 to 1100 °C is adjusted in the fluidized bed reactor. The average solids content amounts to 300 to 600 kg/m³ in the lower zone and to 5 to 50 kg/m³ in the upper zone. The residues from metallurgical plants are preferably fed to the upper zone. If the solid carbon content of the residues from metallurgical plants is insufficient, solid carbonaceous material consisting particularly of coke or anthracite will be added. The expression "a major part" means that distinctly more than 50% of the heat demand are satisfied by a combustion of solid carbon. Part of the heat demand is satisfied by a combustion of reducing gas. Part may be satisfied by a combustion of iron metal if iron metal is contained in the feed. In addition to zinc and lead, alkalies and, e.g., chlorine may be volatilized. Any oil contained in the feed will be vaporized and will act as a fuel. The discharge of the solid material is continuously effected from the lower part of the fluidized bed reactor or from the recycle line. The gas leaving the recycling cyclone is cooled by a spraying of water into the gas and/or by an indirect heat exchange. The temperature required for the reoxida-

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tion of zinc metal will depend on the CO content in the CO-CO₂ mixture. The circulating fluidized bed system consists of the fluidized bed reactor, the recycling cyclone and the recycling line for the solids which have been collected in the recycling cyclone. The term "recycling cyclone" is applicable to one recycling cyclone or to a plurality of recycling cyclones which have gas paths connected in parallel. As distinguished from an "orthodox" fluidized bed, in which a dense phase is separated by a distinct density step from an overlying gas space, the fluidized bed process used for the invention provides in the fluidized bed reactor for states of distribution without a defined boundary layer. There is no density step between a dense phase and an overlying gas space but the solids concentration in the reactor decreases gradually from bottom to top. By means of the Froude and Archimedes numbers the operating conditions can be defined by the following ranges:

$$0.1 \leq \frac{3}{4} \times Fr^2 \times \frac{\rho_s}{\rho_k - \rho_g} \leq 10$$

or $0.01 \leq Ar \leq 100$

wherein

$$Ar = \frac{d_k^3 \times g (\rho_k - \rho_g)}{g_g \times \nu^2} \quad \text{and}$$

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$$Fr^2 = \frac{u^2}{g \times d_k}$$

and

- u = relative velocity of gas in m/s,
 Ar = Archimedes number,
 Fr = Froude number,
 ρ_g = density of gas in kg/m³,
 ρ_k = density of solid particle in kg/m³,
 d_k = diameter of the spherical particle in m,
 ν = kinematic viscosity in m²/s,
 g = constant of gravitation in m/s².

In accordance with a preferred feature, solid carbonaceous material is fed to the lower portion of the fluidized bed reactor below the inlet for the oxygen-containing gases. This will improve the utilization of the carbon in the fluidized bed reactor.

In accordance with a preferred feature the hot solids which have been discharged from the circulating fluidized bed system are subjected to a direct heat exchange with oil-containing moist solids and the resulting vaporization products are fed to the fluidized bed reactor. The oil-containing moist solids which are employed contain virtually no zinc and no lead and consist, e.g., of roll scale. The vaporization products consist of oil, cracked products and water vapor and are preferably fed approximately on the level of the inlet

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for the oxygen-containing gases. As a result the heat content of the solids which have been discharged from the fluidized bed reactor can be utilized for a disposal of such material and the combustible products thus obtained can be utilized in the fluidized bed reactor.

In accordance with a preferred feature the direct heat exchange is effected in an orthodox fluidized bed, in which a fluidization is preferably effected by means of air, which together with the vaporization products is fed as an oxygen-containing gas to the fluidized bed reactor.

In accordance with a preferred feature the direct heat exchange is effected in a mechanical mixer, which may particularly consist of a screw mixer.

In accordance with a preferred feature the exhaust gas from the recycling cyclone has a $\text{CO}:\text{CO}_2$ ratio between 0.3 and 1. That ratio will result in particularly good operating conditions.

In accordance with a preferred feature the fluidizing gas and/or the oxygen-containing gas is preheated by an indirect heat exchange before it enters the fluidized bed reactor. The heating fluid may consist of the exhaust gas from the recycling cyclone before the collection of secondary dust or of the afterburnt exhaust gas after the collection of

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secondary dust. Extraneous heat, e.g., hot gases produced by a combustion of coke oven gas or of gas produced by a steelmaking process, may also be used. As a result, the thermal economy of the process can be improved.

In accordance with a preferred embodiment the feed is preheated by a direct heat exchange with the gas from the recycling cyclone. Preheating is effected in suspension type heat exchangers. This will improve the heat economy of the process.

In accordance with a preferred embodiment, ultrafine residues from metallurgical plants are subjected to a microagglomerating treatment to form agglomerates having a particle size not in excess of 3 mm and are subsequently fed to the circulating fluidized bed system. The microagglomerating treatment may result, e.g., in the production of micropellets. This will result in a more uniform composition of the fluidized bed in the fluidized bed reactor and will facilitate the separation of solids and metal vapor-containing gases.

The invention will now be described more in detail with reference to a drawing and an example.

The circulating fluidized bed system comprises a fluidized bed reactor 1, a recycling cyclone 2 and a recycling line 3. The fluidized bed

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reactor 1 is supplied through line 4 with residues from metallurgical plants and through line 5 with coal. The reducing gas is fed through line 6 to an indirect heat exchanger 7 and is preheated therein and is subsequently fed in line 9 to the fluidized bed reactor 1. Oxygen-containing gas is fed through line 10 to the indirect heat exchanger 11 and is preheated there and is then fed through line 12 as secondary gas to the fluidized bed reactor 1. The lower zone of the fluidized bed in the fluidized bed reactor 1 is operated under more strongly reducing conditions and extends upwardly approximately to the level of the inlet 12 for the oxygen-containing secondary gas. Substantially all solids in the gas-solids suspension discharged from the fluidized bed reactor 1 are removed in the recycling cyclone 2 and the collected solids are recycled in the recycling line 3 to the fluidized bed reactor 1. The gas from the recycling cyclone 2 is fed through a line 13 to an indirect heat exchanger 14 and is cooled therein to a temperature at which zinc metal is oxidized to ZnO. The gas is subsequently fed through line 15 to a dust collector 16. The dustfree gas is discharged by a fan 17 through a line 18. The secondary dust which has been collected in the dust collector 16 is withdrawn in line 19. In a line 20, solids are continuously withdrawn from the lower portion of the fluidized bed reactor

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and fed to the orthodox fluidized bed cooler 21, which is supplied with oil-containing moist solids through line 22 and with an oxygen-containing fluidizing gas through line 24. The fluidizing gas which has been heated up and contains the resulting vaporization products is fed as secondary gas in line 24 to line 12 and further to the fluidized bed reactor 1. Solids are withdrawn from the fluidized bed cooler 21 through line 25.

Example

The fluidized bed reactor had a height of 15 m and was 2.6 m in diameter. The inlet for the oxygen-containing gases was about 4 m above the bottom end of the reactor, the inlet for coal was 3.5 m above that bottom end and the inlet for the residues from metallurgical plants was about 4.5 above said bottom end. The recycling line for the solids collected in the recycling cyclone opened into the fluidized bed reactor on a level which was 5 m above the bottom end of the reactor. The treated solids were withdrawn from the lower zone of the fluidized bed reactor.

The residues from metallurgical plants consisted of a mixture of blast furnace top gas sludge, dust from metallurgical converters and dust collected in a dedusting electrostatic precipitator which succeeds a sintering plant. That mixture had the following composition on a dry basis:

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Fe (total)	57.5%
Fe ²⁺	4.1%
Fe metal	10.1%
Mn	0.8%
P	0.04%
SiO ₂	2.4%
CaO	4.6%
MgO	0.7%
S	0.24%
Pb	0.6%
Zn	1.6%
K ₂ O + Na ₂ O	1.8%
C	4.6%
Cl ⁻	0.6%
ignition loss	4%

The moisture content amounted to 12%.

The fluidized bed reactor was supplied with that mixture at a rate of 20,000 kg/h and with coke having a particle size below 1 mm at a rate of 3,200 kg/h. A fluidizing gas consisting of coke oven gas at a rate of 4,000 standard cubic meters (sm³) per hour was fed to the fluidized bed reactor.

The coke oven gas contained

60.2%	H ₂
25.5%	CH ₄
6 %	CO

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1.5% CO₂
3.4% N₂
3.1% heavy hydrocarbons.

The coke oven gas was preheated in an indirect heat exchanger and at a temperature of 600°C was fed to the fluidized bed reactor, which was supplied at a rate of 11,000 cm³/h with an oxygen-containing gas consisting of air that had been preheated to 750°C by an indirect heat exchange. The temperature in the fluidized bed reactor was adjusted to 1000°C.

The gas leaving the recycling cyclone had the following composition:

3% CO
6% CO₂
11% H₂
35% H₂O
45% N₂

The gas was cooled to 250°C in an indirect heat exchanger and was then passed through a filter, in which secondary dust was collected at a rate of 1,000 kg/h.

The secondary dust contained

26% Zn
10% Pb
40% C

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Solids at a temperature of 1000°C were withdrawn at a rate of 19,200 kg/h from the lower zone of the fluidized bed reactor and were fed to a fluidized bed cooler containing an orthodox fluidized bed. The fluidized bed cooler was fed at a rate of 4,000 kg/h with roll scale sludge that contained water at a rate of 800 kg/h and contained

68% total Fe

4% organic components.

Air at a rate of $1000 \text{ sm}^3/\text{h}$ was fed through the bottom of the fluidized bed cooler and was withdrawn from the fluidized bed cooler at its top and as an oxygen-containing gas was fed to the fluidized bed reactor of the circulating fluidized bed system. Cooled solids at a rate of 23,000 kg/h were withdrawn from the fluidized bed cooler.

Said solids contained

total Fe	58%
Fe metal	0.5%
C	15%
S	0.2%
Zn + Pb	0.1%

The advantages afforded by the invention reside in that a major part of the heat required for the process is generated by a direct combustion of solid

carbon in the fluidized bed itself and a substantial dezincing is nevertheless effected so that a highly economical reprocessing of the residue can be effected.

WHAT IS CLAIMED IS:

1. A method of reprocessing a zinc and lead containing residue from a metallurgical plant comprising:

introducing the residue into a fluidized bed reactor means of a circulating fluidized bed system comprising the reactor means, cyclone means and recycle means;

thermally treating the residue at an elevated
10 temperature and under reducing conditions in said reactor means;

volatilizing zinc and lead;

reducing higher iron oxides as fully as possible
to FeO;

introducing a reducing fluidized gas virtually free of free oxygen into a lower portion of the fluidized bed reactor means;

controlling the rate and composition of the fluidized gas to maintain in the lower portion of the
20 reactor such a reduction potential that at least 80% of the iron content is present as Fe²⁺, not in excess of 1% of the iron content is present as metal iron and the balance being present as Fe³⁺;

introducing a solid carbonaceous material into said reactor means and adjusting the solid carbon content in the lower portion thereof to about 5 to 30%;

supplying an oxygen-containing gas to an upper portion of the reactor means;

supplying a portion of the heat demand for the
30 thermal treatment from the combustion of the carbonaceous

material and forming CO₂ at a rate insufficient to reoxidize zinc metal;

forming a gas-solids suspension in the reactor means and discharging the suspension at an upper portion thereof;

removing solids from said suspension in the cyclone means and recycling the removed solids to the reactor means at a rate per hour equivalent to at least 5 times the weight of the solids contained in the reactor means;

exhausting a cleaned gas from the cyclone means and cooling the gas to a temperature at which zinc metal is oxidized to ZnO; and

removing a dust-like zinc compound and lead compound from the gas.

2. A method according to claim 1, wherein the solid carbonaceous material is fed to the lower portion of the fluidized bed reactor below inlet means for the oxygen-containing gas.

20 3. A method according to claim 1 or 2, wherein hot solids are discharged from the circulating fluidized bed system and are subjected to a direct heat exchange with oil-containing moist solids; and the resulting vaporization products are fed to the reactor means.

4. A method according to claim 3, wherein the direct heat exchange is effected in an orthodox fluidized bed.

5. A method according to claim 3, wherein the direct heat exchange is effected in a mechanical mixer.

6. A method according to claim 1, 2, 4 or 5, wherein the gas from the recycling cyclone contains CO and CO₂ in a CO:CO₂ ratio of (0.3 to 1:1).

7. A method according to claim 1, 2, 4 or 5, wherein the fluidizing gas or the oxygen-containing gas is preheated by an indirect heat exchange before it enters the fluidized bed reactor.

10 8. A method according to claim 1, 2, 4 or 5, wherein the feed is preheated by a direct heat exchange with the gas from the recycling cyclone.

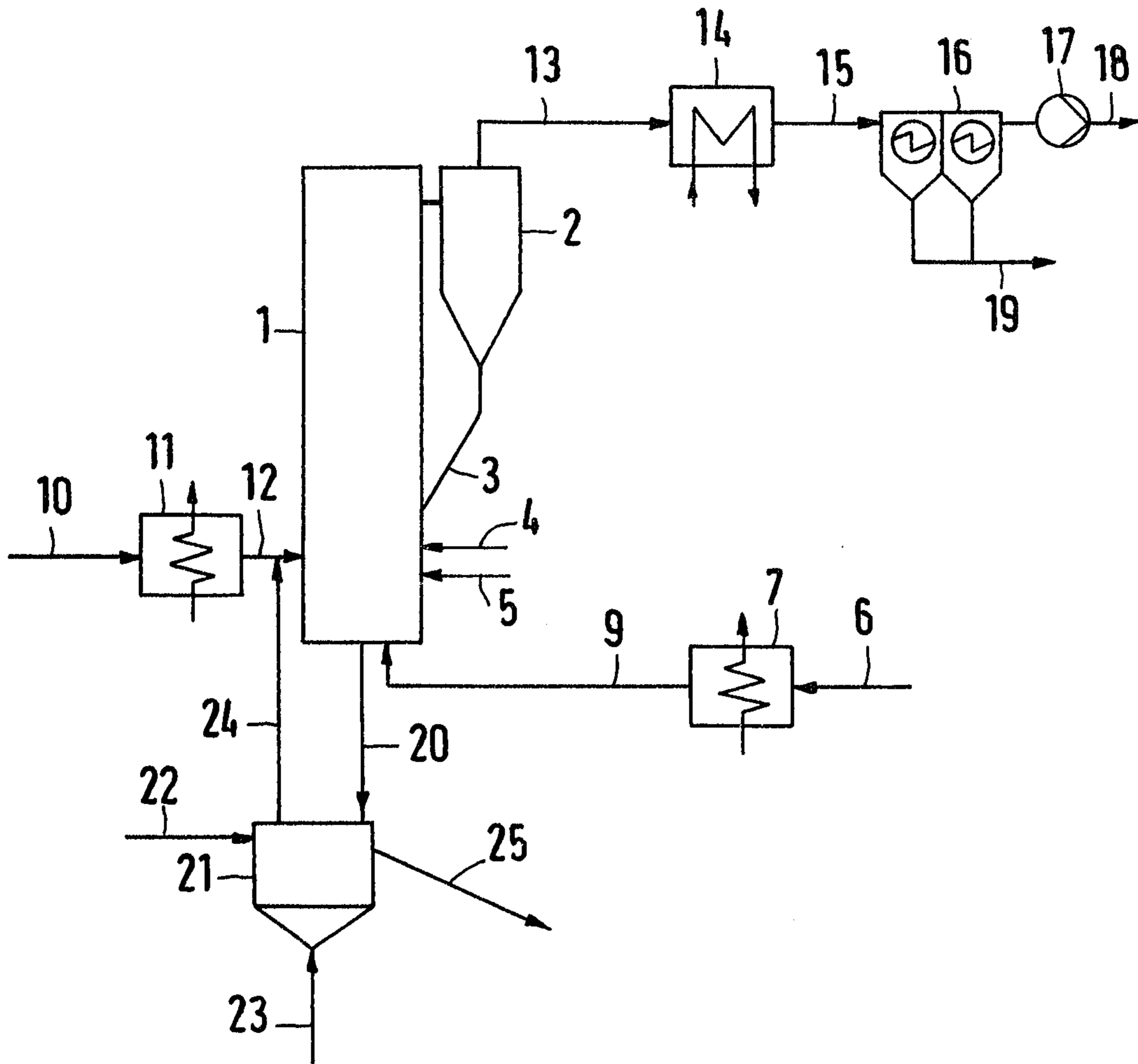
9. A method according to claim 1, 2, 4 or 5, wherein an ultrafine residue is subjected to a micro-agglomerating treatment to form agglomerates having particle size not in excess of 3 mm, the agglomerates being subsequently fed to the circulating fluidized bed system.

20 10. A method according to claim 3, wherein the gas from the recycling cyclone contains CO and CO₂ in a CO:CO₂ ratio of (0.3 to 1:1).

11. A method according to claim 10, wherein the fluidizing gas or the oxygen-containing gas is preheated by an indirect heat exchange before it enters the fluidized bed reactor.

12. A method according to claim 11, wherein the feed is preheated by a direct heat exchange with the gas from the recycling cyclone.

13. A method according to claim 12, wherein an ultrafine residue is subjected to a microagglomerating treatment to form agglomerates having particle size not in excess of 3 mm, the agglomerates being subsequently fed to the circulating fluidized bed system.



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