



(51) International Patent Classification:

C22B 19/38 (2006.01) C22B 19/30 (2006.01)
C22B 4/00 (2006.01) F27B 7/34 (2006.01)
C22B 4/08 (2006.01) F27B 7/36 (2006.01)
C22B 5/12 (2006.01) F27D 17/00 (2025.01)
C22B 5/18 (2006.01) C21B 13/00 (2006.01)
C22B 7/02 (2006.01) C21B 13/08 (2006.01)
C22B 7/04 (2006.01)

(72) Inventors: **LEUCHTENMÜLLER, Manuel**; Montanuniversität Leoben, Franz Josef-Straße 18, 8700 Leoben (AT). **ANTREKOWITSCH, Jürgen**; Montanuniversität Leoben, Franz Josef-Straße 18, 8700 Leoben (AT).

(74) Agent: **VON ROHR PATENTANWÄLTE PARTNERSCHAFT MBB**; Rüttenscheider Straße 62, 45130 Essen (DE).

(21) International Application Number:

PCT/EP2025/060698

(22) International Filing Date:

17 April 2025 (17.04.2025)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

24171075.5 18 April 2024 (18.04.2024) EP

(71) Applicant: **BEFESA STEEL R&D, SOCIEDAD LIMITADA UNIPERSONAL** [ES/ES]; Ctra. Bilbao-Plencia 21, 48950 Erandio, Bizkaia (ES).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CV, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IQ, IR, IS, IT, JM, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, MG, MK, MN, MU, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UY, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, CV, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SC, SD, SL, ST,

(54) Title: METHOD AND PLANT FOR RECYCLING METAL OXIDES

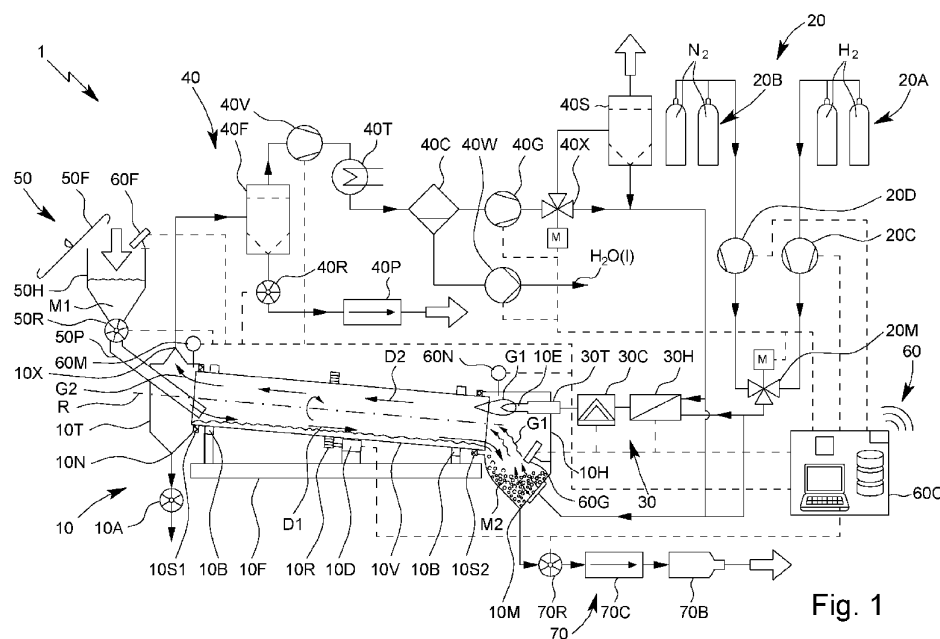


Fig. 1

(57) Abstract: A method and a plant for recycling metal oxides, in particular zinc oxides, from a raw material are proposed, wherein metal oxides are reduced in the raw material by means of hydrogen within a rotary kiln and wherein hydrogen is recovered by reoxidation of gaseous metal with water vapor to hydrogen within the rotary kiln.

SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, ME, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

Published:

- *with international search report (Art. 21(3))*
- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

Method and plant for recycling metal oxides

The present invention relates to a method and a processing/recycling plant for recycling metal oxides, in particular zinc oxides.

5

During the recycling process of coated, in particular galvanized, steel scrap, e.g. by using electric arc furnaces, hereinafter referred to as EAF, hazardous industrial waste material is produced that contains a significant amount of zinc.

10 EP 0 654 538 B1 and EP 1 088 904 B1 disclose a method to recycle such waste material using a pyrometallurgical process that selectively volatilizes zinc oxide to produce high zinc containing secondary raw material, known as Waelz oxide. This recycling process is known as SDHL-Waelz process. However, due to the required coke as reducing agent, the SDHL-Waelz process is carbon based and CO₂ emitting.

15

US 5,013,532 A1 discloses a process for the separation and recovery of zinc, wherein hydrogen is used to reduce zinc oxide to zinc metal. The zinc metal is swept from the furnace dust and reoxidized to zinc oxide with simultaneous regeneration of hydrogen. The hydrogen generated in this way is recycled during this process. However, the process disclosed has several flaws, such as a poor energy efficiency, a poor efficiency regarding the utilization of reduction agent and an insufficient applicability to an industrial-scale plant.

20

WO 98/18971 A1 discloses a method for separation and recovery of metals and metal oxides from industrial minerals and waste materials containing zinc, lead, cadmium, arsenic, iron, mercury and selenium. The metals and metal oxides in dust form are mixed with a reducing agent and additives, agglomerated, heated above 800 °C, and contacted with a flow of inert, reducing or slightly oxidizing gas to volatilize the metals and metal oxides for recovering separate from solid residual product.

30

It is a problem underlying the present invention to provide an improved method and an improved plant for recycling metal oxides, in particular zinc oxides, from a raw material, such as industrial residues, in particular flue dusts, sludges, scales and/or filter cake, preferably wherein an energy-efficient, resource-efficient, efficient regarding reduction agent utilization, scalable, reliable and/or adjustable process is achieved.

35

The problem underlying the invention is solved by a method for recycling metal oxides according to claim 1 and a plant for recycling metal oxides according to claim 19. Advantages further developments are subject to the dependent claims.

5 The plant according to the present invention is adapted to recycle metal oxides, in particular zinc oxides, from raw material, such as industrial residues, in particular flue dusts, sludge, scales, iron ore and/or filter cake, using a process gas containing hydrogen.

10 The plant preferably comprises a rotary kiln, a gas supply system to supply a process gas with hydrogen, a heating system to heat the process gas, a control system to feedback control the components of the plant and an off-gas treatment system to treat off-gas exiting the rotary kiln, in particular to separate particles and water within the off-gas, and to recirculate the treated off-gas back to the heating system.

15 During the course of the research underlying the present invention, several furnace types have been reviewed, including retort furnace, rotary hearth furnace, multiple hearth furnace, shaft furnace, fluidized bed furnace and rotary kiln/furnace.

20 The research found that the rotary kiln is most suitable for recycling of metal oxides using hydrogen, since the rotary kiln can be operated continuously in a counter-current manner and allows for heat recovery and efficient hydrogen utilization, minimal agglomeration requirements and good transport mechanism for volatile matter/components/compounds with the process gas into the off-gas system.

25 A rotary kiln/furnace according to the present invention is a furnace for heating materials to a material heating temperature. The longitudinal axis of the rotary kiln is slightly inclined from the horizontal and, during normal operation, continuously rotates about its longitudinal axis. The rotation of the rotary kiln gradually moves the material within the kiln downward towards the lower end of the rotary kiln in a continuous process.

30

The rotary kiln preferably comprises a charging housing/end for charging of the material to be treated within the rotary kiln, an at least essentially cylindrical rotary kiln body/vessel, a discharge housing/end to discharge the treated material, a refractory lining of the inner walls of the kiln body and/or a drive interacting with the kiln vessel,

35

in particular a gear box and a gear ring attached to the outer wall of the kiln vessel, to rotate the rotary kiln body.

5 The raw material is preferably moved from the upper, charging housing/end to the lower, discharging housing/end into a first direction. The process gas preferably flows from the lower, discharge housing/end towards the upper charging housing/end into a second direction that is opposite to the first direction, i.e. in a counter-current manner.

10 To avoid the contact with the surrounding air, the plant, preferably the rotary kiln, in particular either housings/ends of the rotary kiln body/vessel, is/are gas-tight and/or sealed-off from the surroundings and/or comprises/comprise gas-tight seals.

15 The heating system is preferably adapted to heat the process gas prior entering or within the rotary kiln, in particular the rotary kiln body/vessel, to a gas inlet temperature greater than 1000 °C. To this end, the heating system preferably comprises a heat exchanger, a combustion chamber operated with hydrogen, a heat generator and/or at least one preferably non-transferred plasma torch.

20 The heating system is preferably arranged outside the rotary kiln, in particular its body/vessel. Mostly preferred, the heating system is arranged in or adjacent to the discharging housing. However, the heating system can also be at least partially arranged within the rotary kiln body/vessel.

25 In the method according to the invention, raw material, such as industrial residues, in particular flue dusts, sludges, scales and/or filter cake, are processed by means of a processing/recycling plant to recycle metal oxides, in particular zinc oxides, contained in the raw material in particular solely by means of hydrogen and/or without adding coke or other carbon-containing additives.

30

The method preferably comprises at least one of the following steps:

- 35
- a) feeding the raw material into a charging end/housing of the rotary kiln, preferably in a gas-tight manner;
 - b) heating a process gas comprising hydrogen, preferably of more than 50 vol.-%, 60 vol.-% or 70 vol.-%, mostly preferred of more than 90 vol.-%

% or 95 vol.-%, to a gas inlet temperature greater than 1 000 °C or 1 200 °C, preferably to a gas inlet temperature between 1 300 °C and 1 450 °C;

- 5 c) introducing the process gas into a discharge end/housing of the rotary kiln;
- 10 d) heating the raw material in the rotary kiln, in particular the rotary kiln vessel, (exclusively) by means of the heated process gas, preferably to a (maximum) material heating temperature of less than 1 100 °C and/or greater than 1 000°C, mostly preferred to a (maximum) material heating temperature of at least essentially 1 050 °C;
- 15 e) reducing metal oxides, in particular zinc oxides, of the raw material by means of the hydrogen in the process gas to gaseous metal, in particular zinc, and water vapor in a hotter/reduction section of the rotary kiln, in particular the rotary kiln vessel;
- 20 f) at least partially recovering the hydrogen used/consumed and producing heat by reoxidizing the gaseous metal, in particular zinc, with water vapor to hydrogen and metal oxides, in particular zinc oxides, particles in a colder/reoxidation section of the rotary kiln, in particular the rotary kiln vessel;
- 25 g) emitting off-gas containing the recovered hydrogen and the reoxidized metal oxide, in particular zinc oxide, particles through a gas outlet of the rotary kiln;
- 30 h) treating, in particular cooling, filtering/washing and/or dehumidifying, the off-gas to separate the metal oxide, in particular zinc oxide, particles;
- i) discharging the separated metal oxide, in particular zinc oxide, particles preferably in a gas-tight manner;
- 35 j) recirculating/reintroducing the treated off-gas into the discharge end/housing of the rotary kiln, preferably together with process gas from a gas supply system; and/or
- k) discharging the treated raw material as output material via the discharge end of the rotary kiln.

With the method according to the invention a wide variety of different raw materials can be treated. It is possible to treat raw material with almost no zinc to up to 40 wt.-% zinc or 60 wt.-% zinc.

5 A major aspect of the invention is the recovery of hydrogen consumed for the reduction of metal oxide, in particular zinc oxide, within the rotary kiln through reoxidation by (present) water vapor in the colder/reoxidation section of the rotary kiln.

10 This lowers the hydrogen consumption of the process for a typical high-zinc EAF-dust containing 40 % zinc as zinc oxide and 45 % iron as iron oxide from 25 kg per ton to less than 16 kg per ton EAF-dust. Lowering the amount of hydrogen offers several key benefits, including reduced energy consumption, increased resource efficiency, and easier hydrogen supply. These benefits lead to lower operational and capital expenses, making the process more economically liable and competitive in
15 the market. Additionally, by consuming less hydrogen, the process contributes to a smaller carbon footprint, promoting environmental sustainability.

The rotary kiln ensures that volatile components do not flow through the solid phase of the raw material and can instead exit the rotary kiln seamlessly within the off-gas
20 stream, effectively preventing adherence to the raw material.

In the SDHL-Waelz process, the slag reaches a temperature of up to 1,300 °C. At this temperature sintering and partial melting takes place causing inclusion of valuables that are not available for reduction. This is the reason why zinc oxide partly
25 remains in Waelz slag.

With the present invention, however, the maximum temperature of the raw material can be reduced to 1 100 °C or 1 050 °C which prevents inclusions and allows to nearly
30 fully recover zinc oxide from the slag by maintaining high reduction kinetics/rates.

With the present invention, a direct reduced iron, hereinafter referred to as DRI, can be obtained as output material, having a metallization degree of at least 90 wt.-% and/or having less than 1 wt.-% zinc, mostly preferred less than 0,5 wt.-% zinc.

35 The DRI material can be recycled back, e.g. to EAF, as a scrap substitute.

Another major aspect of the invention is the recovery of heat from the reoxidation of gaseous zinc to (fine-dispersed) zinc oxide particles within the rotary kiln. The gas temperature decreases steadily within the rotary kiln as it heats up the raw material, shifting the thermodynamic equilibrium from the gaseous zinc to zinc oxide and forces reoxidation within the rotary kiln heating up the process gas which in turn heats the rotary kiln and the bulk material.

Preferably, the off-gas composition, in particular the volume fraction of hydrogen and water in the off-gas, is monitored/measured, to calculate the consumption of hydrogen.

The inflow rate and/or the gas inlet temperature are/is then adjusted dependent on the measured gas-composition. In this way, the process can be easily and quickly be adjusted, in particular to changes of the composition of the raw material.

Further, the energy input into the rotary kiln can be adjusted by changing the composition of the process gas. For example, the ratio of the hydrogen to an inert gas within the process gas, such as nitrogen, can be changed so as to adjust the energy input.

The off-gas containing the reoxidized metal oxide particle is emitted out of the rotary kiln through a gas outlet to the off-gas treatment system, preferably wherein the off-gas is subsequently cooled, washed and/or filtered to separate the metal oxide particles from the gas and water vapor.

Further, the (cooled, washed and/or filtered) off-gas is preferably dehumidified to reduce the amount of water within the off-gas.

The treated, in particular cooled, washed, filtered and/or dehumidified, off-gas is preferably recirculated to the rotary kiln, in particular via the heating system and/or the bulk of output material in the discharge housing of the rotary kiln.

In this way, the hydrogen consumption and the energy consumption can be significantly reduced, as already explained.

The water used for the recovery of the hydrogen in the rotary kiln is preferably solely obtained through the reduction process within the rotary kiln. With other words, preferably no additional water is added to the process, in particular the rotary kiln.

5 According to a preferred method variant, at least a part of the process gas is directly or indirectly (pre)heated by means of the (hot) output material, in particular prior entering the rotary kiln. For example, part of the process gas can be directed through the output material, in particular the bulk of the output material collected in the discharge housing. Alternatively or in addition, part of the process gas can be indirectly
10 heated by means of the (hot) output material, e.g. by means of a heat exchanger. With other words, the output material is preferably cooled by means of the process gas.

15 In this way, the heat in the output material can be at least partially recovered and the energy consumption of the process can be further reduced.

Thus, in the method according to the present invention, metal oxides are recycled in a particular energy-efficient and resource-efficient manner, wherein the energy and hydrogen consumption is reduced due to the heat and hydrogen recovery within the
20 colder section of the rotary kiln. The process can be easily and quickly adapted to different kinds of raw material and allows a recycling process on a large industrial scale.

25 Another aspect of the present invention relates to a plant for recycling metal oxides, in particular zinc oxides, from raw material, wherein the plant is adapted to carry out the method, in particular individual or all method steps, as described above. In this way, corresponding advantages can be achieved.

30 The aforementioned aspects, features and method steps of the present invention as well as the aspects, features and method step of the present invention resulting from the claims and the following description, can – in principle – be realized independently of one another but also in any combination or sequence.

35 Further aspects, advantages, features and characteristics of the present invention are apparent from the claims and the following description of a preferred embodiment with reference to the figures.

- Fig. 1 shows a schematic piping and instrumentation diagram of the plant comprising a rotary kiln according to the invention;
- 5 Fig. 2 shows in a schematic diagram the temperature change of the process gas and the raw material over the length of the rotary kiln of the plant according to Fig. 1;
- Fig. 3 illustrates the basic chemical processes within the rotary kiln;
- 10 Fig. 4 shows in a schematic diagram the changes of the composition of the process gas over the length of the rotary kiln; and
- Fig. 5 shows in a schematic diagram the changes of the composition of the raw material over the length of the rotary kiln.

15

In the partly not to scale, only schematic figures, the same reference signs are used for identical or similar parts and components, resulting in corresponding or comparable properties and advantages, even if a repeated description is omitted.

20

Fig. 1 is a schematic piping and instrumentation diagram of a processing/recycling plant 1, hereinafter referred to as plant 1, according to a preferred embodiment of the present invention.

25

The plant 1 is adapted to recycle metal oxides, in particular zinc oxides, hereinafter referred to as ZnO, from a raw/source material M1. The plant 1 is preferably adapted to process industrial residues, in particular flue dusts, sludges, scales, iron ore and/or filter cakes, as raw material M1 so as to recycle metal oxides, in particular ZnO, contained therein preferably solely using hydrogen, hereinafter referred to as H₂, as will be explained in the following.

30

In the following, the recycling of ZnO will be described. However, the plant 1 and the method can also be used to recycle other metal oxides, even if this is not repeatedly mentioned.

35

The plant 1 comprises a furnace in form of a rotary kiln 10, a gas supply system 20 to supply a process gas G1, a heating system 30 to heat the process gas G1, an off-gas treatment system 40 to treat the off-gas exiting the rotary kiln 10, a raw material

supply system 50 to supply the raw material M1 to the rotary kiln 10, a material output system 70 to discharge, convey and/or transport the treated raw material M1 and/or a control system 60 to monitor and (feedback) control one or more components of the plant 1.

5

The rotary kiln 10 preferably comprises a charging housing/hood 10T forming an inlet/charging end of the rotary kiln 10 through which the rotary kiln 10 can be charged with the raw material M1 supplied by the raw material supply system 50.

10

Further, the rotary kiln 10 comprises a discharge housing/hood 10H forming an outlet/discharge end of the rotary kiln 10 through which the treated raw material M1 can be discharged as output material M2.

15

The discharge housing/hood 10H, hereinafter referred to as discharge housing 10H, is preferably embodied as elongated/vertical funnel. The discharge housing 10H preferably comprises or forms a material outlet 10M at its lower end and/or a gas inlet 10E at its upper end.

20

A main component of the rotary kiln 10 is the at least essentially cylindrical rotary kiln body/vessel 10V, hereinafter referred to as vessel 10V.

25

The vessel 10V is at least essentially embodied as an elongated hollow cylinder extending from the charging housing 10T to the discharge housing 10H. As indicated in Fig. 1, the vessel 10V preferably extends laterally into the discharge housing 10H, preferably from a side that is opposite to the gas inlet 10E.

30

The rotary kiln 10, in particular the vessel 10V, preferably comprises a length of at least 30 meters or 40 meters and/or of at most 120 meters, 100 meters or 80 meters.

35

The rotary kiln 10 is preferably adapted to heat the raw material M1 from a material inlet temperature T_{M1} to a material heating temperature T_{M2} while conveying the raw material M1 from the charging end towards the discharge end or housing 10H. For this purpose, the rotary kiln 10, in particular the vessel 10V, mostly preferred its main/rotation axis R, is inclined from the horizontal, preferably by an angle of at least 1° or 2° and/or at most 5° or 4° , in particular between 1° to 3° .

The rotary kiln 10, in particular the inner wall of the vessel 10V, preferably comprises a refractory lining, e.g., made out of high temperature insulating bricks, to insulate the wall of the vessel 10V from the temperatures inside the vessel 10V and to achieve the required heat and wear resistance.

5

The rotary kiln 10 preferably comprises a drive 10D, preferably in form of an electric motor, to rotate the vessel 10V around the rotation axis R. The vessel 10V, in particular its outer wall, can be equipped with a gear ring 10R through which the drive 10D can directly or indirectly, e.g., via a gear box (not shown), transfer a torque.

10

The rotary kiln 10, in particular the vessel 10V, preferably rotates with a rotation speed of more than 0,2 or 0,5 and/or less than 3 or 1,5 revolutions per minute, mostly preferred between 0,8 to 1,5 revolutions per minute.

15

The rotary kiln 10 is preferably further equipped with a basis 10F, such as a concrete foundation, a metal frame and/or a roller station, and at least two bearings 10B, wherein the vessel 10V is rotatably mounted onto the basis 10F via the bearings 10B.

20

To prevent or minimize gas exchange with the atmosphere, the plant 1, preferably all gas-carrying components, in particular the rotary kiln 10, is/are preferably at least essentially gastight and/or sealed off from its surroundings. To this end, the plant 1, in particular the rotary kiln 10, preferably comprises a sealing system and/or a plurality of seals 10S1, 10S2.

25

As indicated in Fig. 1, the rotary kiln 10 preferably comprises a first seal 10S1 arranged between the charging housing 10T and a first end of the vessel 10V to seal off the connection between the charging housing 10T and the vessel 10V and a second seal 10S2 between the discharge housing 10H and the second end of the vessel 10V to seal off the connection between the discharge housing 10H and the vessel 10V.

30

The sealing system, in particular the seals 10S1, 10S2, can be operated by using a seal gas. In particular, the seals 10S1, 10S2 can be supplied by the additive gas, such as N₂ or Ar, e.g., from the gas supply system 20, to seal off the plant 1, in particular the rotary kiln 10, from its surroundings.

35

As already mentioned, the plant 1 preferably comprises a raw material supply system 50.

5 The raw material supply system 50 is preferably adapted to supply raw material M1 into the rotary kiln 10, in particular to the inlet of the vessel 10V, mostly preferred in a continuous manner.

10 The raw material supply system 50 preferably comprises one or more closed storages or bunkers containing the raw material M1, e.g. as pellets, lumps or in a semi-solid form.

The raw material M1 is preferably an industrial, metal-bearing, in particular zinc-bearing, residue, in particular dust from EAF and/or residue of battery production and/or recycling, sludge, scale, iron ore, and/or filter cake.

15 The raw material M1 may be (pre-)treated or untreated.

20 Optionally, the raw material supply system 50 can include a treatment system (not shown) comprising one or more treatment apparatuses to treat the raw material M1 prior supplying the material M1 to the rotary kiln 10.

25 The treatment system can be equipped with a mixer to mix/homogenize the raw material M1 with additives or binders, e.g. water, molasses, starch, or lime, depending on the composition of the raw material M1. Further, the treatment system can be equipped with a dehumidifying or humidifying unit to adjust the water content within the raw material M1. Optionally, the treatment system may include a forming apparatus for pelletizing or briquetting of the raw material M1.

30 Typical average values for the chemical composition of industrial residues that can be used/processed in the plant 1 are shown in the table below:

Component	Dust from carbon/low alloyed steel production (wt.-%)	Dust from alloy steel production (wt.-%)	Dust from stainless steel production (wt.-%)
Fe _{tot}	10 – 45	17 – 37	20 – 65
SiO ₂	0.6 – 5.1	1.7 – 5	3 – 9
CaO	3 – 17	2 – 16	8 – 20
Al ₂ O ₃	0.3 – 3	1 – 4	0.4 – 2
MgO	0.5 – 6	1.2 – 3	1 – 5
P ₂ O ₅	0.1 – 0.37	0.01 – 0.1	0.03 – 0.1
MnO	1.1 – 6	1.5 – 6.9	2.2 – 6.3
Cr ₂ O ₃	0.13 – 2	0.12 – 6	9 – 20
Na ₂ O	0.3 – 3	Not available	0.6 – 2
K ₂ O	0.5 – 2.3	Not available	0.7 – 3
Zn	21 – 43	2 – 15	2 – 25
Pb	0.4 – 10	0.05 – 3.6	0.2 – 4.5
Cd	0.02 – 0.18	0.01 – 0.04	0.01 – 0.08
Cu	0.08 – 0.5	0.01 – 0.8	0.015 – 0.5
Ni	0.01 – 0.8	0.01 – 0.5	1 – 8
V	0.01 – 0.09	0.01 – 0.2	0.05 – 0.12
W	Not available	0.5 – 1.5	Not available
Co	0.001 – 0.01	0.01 – 0.2	0.02 – 0.04
As	0.001 – 0.02	0.001 – 0.01	0.01
Hg	0.0001 – 0.005	0.05 – 0.7	0.0002 – 0.015
Cl	0.8 – 5	0.7 – 1.7	0.8 – 1
F	0.02 – 0.9	0.01 – 0.65	0.3 – 2.4
S	0.1 – 3	0.25 – 1.42	0.2 – 0.5
C	0.4 – 3.3	0.5 – 3.1	0.05 – 1.3
Basicity	2.0 – 6.5	Not available	Not available
Moisture	6 – 16	Not available	Not available

The raw material supply system 50 preferably comprises a feeding apparatus 50F, a charging/storage hopper 50H, a (rotary) airlock (feeder) 50R and/or an inlet chute 50P.

The feeding apparatus 50F is adapted to feed the raw material M1, e.g. from a bunker (not shown), to the charging hopper 50H. The feeding apparatus 50F might be embodied as an (inclined) elevator. However, other solutions are possible as well.

5 The charging hopper 50H is connected to the charging housing 10T of the rotary kiln 10, in particular an inlet of the vessel 10V, via the airlock 50R and/or the inlet chute 50P.

10 The airlock (feeder) 50R is adapted to – continuously or in batches - feed in the raw material M1 and/or charge the rotary kiln 10 in a gas-tight manner, in particular from the charging hopper 50H to the charging housing 10T. Preferably, the airlock 50R is embodied as a rotary airlock feeder/valve. However, other solutions are possible as well.

15 The inlet chute 50P is preferably embodied as a down pipe. However, other solutions are possible as well.

20 As already mentioned, the rotary kiln 10 is preferably adapted to convey the raw material M1 from the inlet/charging end towards the outlet/discharge end of the rotary kiln 10 into a first direction D1.

25 The rotary kiln 10 is preferably operated in a counter-current manner. The process gas G1 flows from the outlet/discharge end towards the inlet/charging end into a second direction D2 that is opposite to the first direction D1.

30 Within the rotary kiln 10, in particular the vessel 10V, the raw material M1 is heated and undergoes several reduction steps, as will be explained further below with reference to Figs. 2 to 5.

35 The treated raw material M1 is discharged as output material M2 via the material outlet 10M of the discharge housing 10H.

As already mentioned, the plant 1 preferably comprises an optional material output system 70.

35 The material output system 70 is preferably adapted to discharge, convey, temporarily store and/or post-treat the output material M2.

The plant 1, in particular the material output system 70, is preferably equipped with a (rotary) airlock (feeder) 70R, a material conveyor 70C and/or a briquetting machine/press 70B.

5

The airlock (feeder) 70R is adapted to – continuously or in batches - feed in the output material M2 and/or discharge the rotary kiln 10, in particular the discharge housing 10H, in a gas-tight manner, in particular to the conveyor 70C. Preferably, the airlock 70R is embodied as a rotary airlock feeder/valve. However, other solutions are possible as well.

10

The material conveyor 70C is adapted to convey the output material M2 to a bunker (not shown) and/or for treatment of the output material M2.

The optional briquetting machine/press 70B is adapted to pressurize and form the output material M2 to briquettes.

15

As already mentioned, the plant 1 comprises a gas supply system 20 to supply the process gas G1 to the rotary kiln 10, in particular to the discharge end thereof.

20

The gas supply system 20 comprises a (first) gas storage 20A containing H₂. Further, the gas supply system 20 can be equipped with a (second) gas storage 20B containing an additive gas, preferably an inert gas, such as nitrogen, hereinafter referred to as N₂, or argon, hereinafter referred to as Ar, in particular to flush the gas-conducting components of the plant 1, mostly preferred when putting the plant 1 into operation, e.g., after maintenance.

25

In the present embodiment each gas storage 20A, 20B is formed by a plurality of gas bottles, preferably wherein the gas is pressurized within each gas bottle. However, other solutions are possible as well.

30

Mostly preferred the gas storage 20A, 20B comprises compressed gas, i.e. the gas contained in each gas storage 20A, 20B is kept under pressure, preferably of at least 10 MPa or 30 MPa and/or at most 80 MPa or 70 MPa. However, it is also possible that the gas storage 20A and/or the gas storage 20B contain/contains liquified gas, preferably at a temperature of less than -150 °C or less than -200 °C, in particular less than -250 °C.

35

5 The gas supply system 20 preferably comprises a (first) compressor/fan 20C to transport H₂ from the (first) gas storage 20A to the heating system 30 and/or a (second) compressor/fan 20D to transport the additive gas, in particular N₂ or Ar, from the second gas storage 20B to the heating system 30.

10 Optionally, the gas supply system 20 can be equipped with a mixing device 20M to mix H₂ with the additive gas to provide the (premixed) process gas G1 to the heating system 30.

The heating system 30 is preferably adapted to heat H₂ and optionally the additive gas or the premixed process gas G1 to a gas inlet temperature T_{G1}.

15 The gas inlet temperature T_{G1} is preferably the (average) temperature of the process gas G1 at the outlet of the heating system 30, within the discharge housing 10H, at the gas inlet 10E of the rotary kiln 10 and/or immediately before entry into the vessel 10V. Preferably, the gas inlet temperature T_{G1} is the highest temperature of the process gas G1 during the process.

20 The gas inlet temperature T_{G1} is preferably greater than 1 000 °C or 1 200 °C, mostly preferred greater than 1 300 °C, and/or less than 1 600 °C or 1 500 °C.

The gas inlet temperature T_{G1} is preferably measured by means of a temperature sensor, such as a thermocouple.

25 The heating system 30 preferably comprises an optional (direct or indirect) heat exchanger 30H to preheat H₂, the additive gas and/or the (premixed) process gas G1 to a temperature of more than 200 °C, preferably more than 500 °C or 800 °C, and/or less than 1 000 °C.

30 The heating system 30 preferably comprises an optional combustion chamber 30C. The combustion chamber 30C is preferably operated with H₂ from the gas storage 20A and/or with the (treated) off-gas G2 from the off-gas treatment system 40. Alternatively or in addition, the heating system 30 comprises an electrically operated heating chamber to heat the process gas G1 to a gas inlet temperature T_{G1} greater than 1 100 °C

35

In addition or alternatively, the heating system 30 can be equipped with at least one burner, in particular a plasma torch 30T, to heat the process gas G1 to the gas inlet temperature T_{G1} .

- 5 The plasma torch 30T is preferably embodied as a non-transferred direct current plasma torch.

10 The plasma torch 30T is adapted to generate a direct flow of plasma, i.e. a plasma jet. Mostly preferred, the heating system 30 comprises a plurality of plasma torches 30T arranged parallel to one another and/or around the gas inlet 10E to evenly heat the stream of the process gas G1, in particular flowing into the discharge housing 10H via the gas inlet 10E.

15 The heating system 30, in particular the plasma torch 30T, can be partially or completely arranged within the rotary kiln 10, in particular the discharge housing 10H and/or vessel 10V. In this way, heat losses are reduced and a compact design is achieved. However, the entire heating system 30 might also be arranged outside and/or at a distance from the rotary kiln 10.

20 As already mentioned, the process gas G1 flows through the rotary kiln 10 in the second direction D2 towards the charging end of the rotary kiln 10. Within the rotary kiln 10, in particular the vessel 10V, the process gas G1 reduces metal oxides, in particular ZnO, of the raw material M1, by means of the H_2 to gaseous metal, in particular zinc, hereinafter referred to as Zn, and water vapor, as will be explained in
25 detail below.

30 The rotary kiln 10, in particular the charging housing 10T, preferably comprises a gas outlet 10X for emitting of the off-gas G2. The gas outlet 10X is preferably arranged at an upper side of the charging housing 10T.

35 The charging housing 10T preferably comprises a dust outlet 10N for deposition of dust, i.e. heavy particles, caused by the carry-over of the gas stream. Thus, the charging housing 10T preferably comprises or forms an integrated settling chamber to collect dust, i.e. heavy particles, that can be recycled to the rotary kiln 10. Preferably, the charging housing 10T is embodied as an elongated/vertical funnel, wherein the dust outlet 10N is arranged at the lower end of the funnel.

Optionally, the rotary kiln 10 can be equipped with a (rotary) airlock (feeder) 10A. The dust/particles collected in the charging housing 10T can be fed out by means of the airlock 10A in a gas-tight manner.

5 The airlock (feeder) 10A is adapted to – continuously or in batches - feed out the dust/particles and/or discharge the charging housing 10T in a gas-tight manner. Preferably, the airlock 10A is embodied as a rotary airlock feeder/valve. However, other solutions are possible as well.

10 The off-gas treatment system 40 is adapted to treat the off-gas G2 exiting the rotary kiln 10 and to recirculate the treated off-gas G2 back to the heating system 30 and/or to the discharge housing 10H.

15 The off-gas treatment system 40 preferably comprises an optional off-gas compressor/fan 40V, a filter apparatus 40F, a cooling apparatus 40T, a (rotary) airlock (feeder) 40R, a product conveyor 40P, a condenser/dehumidifier 40C, a pump 40W, a treated gas compressor/fan 40G, an exhaust 40X and/or a treatment unit 40S.

20 The off-gas compressor/fan 40V is preferably adapted to transport the off-gas G2 from the gas outlet 10X towards the cooling apparatus 40T, filter apparatus 40F and/or condenser/dehumidifier 40C.

25 Instead of several compressors/fans 20D, 20C, 40V, 40G arranged at different locations, the plant 1 might also be equipped with one (central) compressor/fan (station/arrangement), e.g., located between the inlet of the (premixed) process gas G1 and/or the off-gas treatment system 40, in particular the condenser 40C, on the one side and the heating system 30 on the other side. In case of a central compressor/fan station/arrangement, several compressors/fans can be connected in parallel.

30 The filter apparatus 40F is preferably adapted to filter/wash, in particular de-dust, the off-gas G2. The filter apparatus 40F can be embodied as a cyclone separator, a bag filter, a ceramic filter, a venturi washer or as a gas scrubber.

35 The filter apparatus 40F is preferably adapted to separate the solid/fine dispersed metal oxide particles from the gaseous H₂ and/or water vapor.

The separated/crude metal oxide, in particular ZnO, particles can then be fed out by means of the airlock 50R in a gas-tight manner and/or transported/conveyed by means of the product conveyor 40P for storage or direct further processing.

5 The airlock (feeder) 40R is adapted to – continuously or in batches – feed out the separated/crude metal oxide, in particular ZnO, particles and/or discharge the filter apparatus 40F in a gas-tight manner. Preferably, the airlock 50R is embodied as a rotary airlock feeder/valve. However, other solutions are possible as well.

10 The cooling apparatus 40T is adapted to lower the temperature of the (filtered) off-gas G2, preferably to less than 200 °C or less than 100 °C.

As indicated in Fig. 1, the cooling apparatus 40T can be embodied as a heat exchanger, preferably using water as coolant. Alternatively, the cooling apparatus 40T
15 can be embodied as a cooling line, e.g., a double pipe with optional water injection.

The cooling apparatus 40T may be arranged directly downstream of the rotary kiln 10, in particular its charging housing 10T, and/or upstream of the filter apparatus 40F.
20

The condenser 40C is adapted to condense the treated, in particular cooled and filtered, off-gas G2 to dehumidify the off-gas G2 and/or to condense H₂O(g) to H₂O(l).

25 Instead of or in addition to the condenser 40C, a heat exchanger and/or a demister could be used.

The pump 40P is adapted to pump the water obtained in this way out of the plant 1 and/or for further processing. In particular, the water obtained in this way may be used to humidify the raw material M1 in the humidifier of the raw material supply
30 system 50.

The treated gas compressor/fan 40G is adapted to transport the treated, in particular cooled, filtered and/or dehumidified, off-gas G2 back to the heating system 30.

35 In this way, the H₂ consumption can be significantly reduced, as already explained.

As already mentioned, the plant 1, in particular the off-gas treatment system 40, can be equipped with an exhaust 40X and/or a treatment unit 40S.

5 The treatment unit 40S is preferably adapted to treat and/or capture / filtered out contaminants/impurities, in particular carbon monoxide, hereinafter referred to as CO, carbon dioxide, hereinafter referred to as CO₂, and/or sulphur dioxide, hereinafter referred to as SO₂, in the off-gas G2, mostly preferred by means of adsorption, carbon scrubbing and/or membrane gas separation. To this end, the treatment unit 40S can be equipped with a carbon dioxide scrubber and/or a gas separation mem-
10 brane.

By means of the exhaust 40X the treated, in particular cooled, filtered/washed and/or dehumidified, off-gas G2 can be (when necessary) directed to the treatment unit 40S, in particular for further treatment, e.g. for carbon capture, in particular depending on
15 the concentration of the contaminants/impurities.

Alternatively, the treated, in particular cooled, filtered/washed and/or dehumidified, off-gas G2 can be discharged out of the plant 1 into the environment, e.g. via a chimney (not shown).
20

Preferably, some or all components of the plant 1, in particular of the rotary kiln 10, the gas supply system 20, the heating system 30, the off-gas treatment system 40, the raw material supply system 50 and/or the material output system 70, are feed-back controlled.
25

Further, some process parameters, in particular the feed/mass flow rate m_{M1} of the raw material M1, the output/mass flow rate m_{M2} of the output material M2, the material heating temperature T_{M2} of the output material M2, the gas inlet temperature T_{G1} of the process gas G1, the gas outlet temperature T_{G2} of the off-gas G2, the inflow rate
30 V_{G1} of the process gas G1, the outflow rate V_{G2} of the off-gas G2, the consumption rate of H₂ within the rotary kiln 10, the rotation speed of the rotary kiln 10 and/or the pressure within the rotary kiln 10, are directly or indirectly measured and/or calculated and/or used to (feedback) control some or all components of the plant 1.

35 To this end, the plant 1 is equipped with the control system 60 that comprises a control unit 60C and a plurality of measuring devices 60M, 60N, 60F and 60G.

The control unit 60C preferably comprises a data processing device, a control device and/or a communication device.

5 The control system 60, in particular the control unit 60C, is preferably electrically connected to one more components of the plant 1, as indicated by dashed lines in Fig. 1.

10 The control unit 60C, in particular the data processing device, is preferably a device for evaluating, storing and/or processing one or more signals, data, measured values, reference values, information or the like. In particular, the data processing device has a computer unit, such as a processor, and/or a (data) storage/memory, for example in form of an SSD.

15 By means of the communication device, the control system 60, in particular the control unit 60C, can be data-connected with one or more (external) devices, in particular a mobile device, such as a mobile phone, and/or apparatus, in particular a central apparatus, such as a server.

20 By means of the measuring devices 60M, 60N, 60F and 60G one or more variables/parameters can be determined/measured (directly or indirectly). For this purpose, the measuring devices 60M, 60N, 60F and 60G have one or more sensors and/or measuring units, such as a temperature sensor, e.g., a thermocouple, a thermographic camera, a pressure sensor, a rotational speed measuring unit, a humidity sensor, a weight sensor, a gas flow meter, a mass flow meter, an ultrasonic flow
25 meter, an anemometer, a gas detector, in particular a chromatography detector, a flame ionization detector, a mass spectrometer, a FTIR spectrometer, or a thermal conductivity detector, or the like.

30 In the present embodiment, a first measuring device 60M is preferably arranged at the charging end and a second measuring device 60N is arranged at the discharge end of the rotary kiln 10.

35 The first measuring device 60M is preferably adapted to directly or indirectly measure/quantify the off-gas G2 composition, in particular the H₂ and/or H₂O concentration, e.g. by using mass spectrometry, and/or to measure the gas outlet temperature T_{G2}.

The second measuring device 60N is preferably adapted to measure the gas inlet temperature T_{G1} .

5 The control system 60 preferably comprises a third measuring device 60F to (directly or indirectly) measure the feed/mass flow rate m_{M1} , e.g. by monitoring the fill level of the feed bunker or the charging hopper 50H.

10 Further, the control system 60 might be equipped with a fourth measuring device 60G to measure the output/mass flow rate m_{M2} of the output material M2, e.g. by monitoring the output material M2 weight or the fill level of an output material bunker or the discharge housing 10H.

15 By means of the measured/determined values/parameters it is possible to calculate the consumption of H_2 . Based on the H_2 consumption rate and the composition of the raw material M1 it is possible to adjust the feed rate m_{M1} of the raw material M1, the composition of the process gas G1, the inflow rate V_{G1} and/or the gas inlet temperature T_{G1} of the process gas G1, in particular by controlling the gas supply system 20, preferably the first compressor/fan 20C, the second compressor/fan 20D, the mixing device 20M, and/or the heating system 30 and/or the raw material supply
20 system 50.

In the following the proposed method will be described with reference to Fig. 1. Afterwards, the reaction mechanisms within the rotary kiln 10 will be described with reference to Fig. 2 to 5.

25 The proposed method for recycling metal oxides, in particular ZnO, from the raw material M1 is preferably carried out by and/or in the plant 1, in particular by means of the rotary kiln 10, the gas supply system 20, the heating system 30, the off-gas treatment system 40, the raw material supply system 50, the control system 60
30 and/or the material output system 70.

The method is preferably designed as a multi-stage and/or multi-step method. In particular, the method has several method steps that can – in principle – be implemented independently of each other, but also in any sequence and/or combination
35 unless otherwise specified in the following.

In a first optional method step, the composition of the process gas G1 is adjusted, in particular by means of the control system 60 and/or the mixing device 20M.

5 To this end, H₂ is preferably fed from the first gas storage 20A towards the mixing device 20M by means of the first compressor/fan 20C and the additive gas is fed from the second gas storage 20B towards the mixing device 20M by means of the second compressor/fan 20D.

10 The (premixed) process gas G1 preferably comprises more than 50 vol.-%, 60 vol.-% or 70 vol.-%, mostly preferred more than 90 vol.-% or 95 vol.-%, H₂ and/or less than 50 vol.-%, 40 vol.-% or 30 vol.-%, mostly preferred less than 10 vol.-% or 5 vol.-%, H₂O.

15 The (premixed) process gas G1 preferably contains/comprises more than 40 wt.-%, 50 wt.-%, 60 wt.-% or 90 wt.-% H₂, mostly preferred more than 95 wt.-% H₂ or 99 wt.-% H₂.

20 In a further/second method step, the (adjusted/premixed) process gas G1 is fed towards the heating system 30, in particular the heat exchanger 30H, the combustion chamber 30C and/or the plasma torch 30T, to heat the process gas G1 to the gas inlet temperature T_{G1} of more than 1000 °C, in particular of more than 1200 °C, mostly preferred between 1200 °C and 1400 °C.

25 The process gas G1 can be heated by means of the plasma torch 30T.

Alternatively or in addition, the process gas G1 can be heated by partial combustion of H₂ in the process gas G1, in particular by combusting of more than 1 vol.-% and/or less than 10 vol.-% of H₂ in the process gas G1. However, it is also possible to at least partially burn the recirculated off-gas G2.

30 It is preferred that the process gas G1 is heated prior entering the rotary kiln 10. However, the process gas G1 may also be heated to the gas inlet temperature T_{G1} within the rotary kiln 10, in particular the discharge housing 10H and/or the vessel 10V.

35 In a further method step, the (heated) process gas G1 is introduced into the rotary kiln 10, in particular its discharge housing 10H and/or via the gas inlet 10E.

According to a preferred method variant, at least a part of the process gas G1, in particular more than 50 vol.-% or 60 vol.-% of the process gas G1, is directly or indirectly (pre)heated by means of the (hot) output material M2, in particular prior entering the rotary kiln 10.

Preferably, at least a part of the process gas G1 is directed through the output material M2, in particular the bulk of the output material M2 that is collected and/or temporarily stored in the discharge housing 10H, preferably in front of the airlock 70R.

Mostly preferred, at least a part of the process gas G1 is introduced into a lower end of the discharge housing 10H, the process gas G1 subsequently flowing upwards, through the output material M2, towards the gas inlet 10E and/or towards the stream of the (other) part of the process gas G1 exiting the heating system 30. To this end, the discharge housing 10H preferably comprises an additional gas inlet at its lower end, as indicated in Fig. 1.

Thus, at least a part of the process gas G1 is preferably directly preheated by means of the output material M2 prior entering the rotary kiln 10, in particular the vessel 10V, preferably to a temperature of more than 700 °C or 900 °C, mostly preferred at least essentially to the temperature of the output material M2, e.g. to at least essentially 1 000 °C. Simultaneously, the output material M2, in particular the output material M2 that is collected and/or temporarily stored in the discharge housing 10H, is cooled by means of process gas G1 flowing therethrough, preferably to a temperature of less than 900 °C or 800 °C, in particular less than 700 °C or 500 °C.

The process gas G1 flowing through the output material M2 is preferably subsequently heated by means of the heating system 30, in particular the plasma torch 30T, and/or by means of the (part of the) process gas G1 exiting the heating system 30, in particular the plasma torch 30T, mostly preferred to the gas inlet temperature T_{G1} .

With other words, a (first) part/flow of the process gas G1 is preferably directed through and/or directly heated by means of the heating system 30 whereas a (second) part/flow of the process gas G1 preferably bypasses the heating system 30 and/or is preferably directed through and/or directly heated by means of the output material M2. Subsequently, the first part/flow of the process gas G1 and the second

part/flow of the process gas G1 are mixed, preferably within the rotary kiln 10, in particular the discharge housing 10H, mostly preferred such that the temperature of the mixed process gas G1 corresponds to the (desired) gas inlet temperature T_{G1} .

5 Alternatively or in addition, at least a part of the process gas G1 can be indirectly heated by means of the (hot) output material M2, in particular in a heat exchanger. For example, the heat exchanger 30H might be adapted to indirectly heat (part of) the process gas G1 by means of the heat of the output material M2.

10 In this way, the heat of the output material M2 can be efficiently used to preheat the process gas G1.

The process gas G1 flows through the rotary kiln 10, in particular its vessel 10V, into the second direction D2 and/or from the discharge housing 10H towards the charging housing 10T, in particular its gas outlet 10X.
15

During a further method step and/or simultaneously, the optionally pre-treated raw material M1 is fed into the rotary kiln 10, in particular its charging housing 10T, preferably by means of the raw material supply system 50, in particular its charging hopper 50H, the airlock 50R and/or inlet chute 50P, mostly preferred in a continuous and/or gas-tight manner.
20

The raw material M1 is conveyed from the charging end towards the discharge end of the rotary kiln 10 and/or into the first direction D1 that is opposite the second direction D2.
25

It is preferred that the raw material M1 is not preheated prior entering the rotary kiln 10. However, in principle, the raw material M1 can also be preheated, e.g. by using exhaust/waste heat of the plant 1.
30

Thus, the material inlet temperature T_{M1} of the raw material M1 preferably corresponds at least essentially to the ambient temperature and/or is greater than 0 °C and/or lower than 40 °C.

35 In the rotary kiln 10, in particular its vessel 10V, heat is transferred from the process gas G1 to the raw material M1, mostly preferred by thermal convection and thermal conduction.

Thus, the raw material M1 is heated within the rotary kiln 10 by means of the process gas G1 whereas the process gas G1 is cooled by means of the raw material M1.

5 Fig. 2 shows in a schematic diagram the profiles of the temperature of the material M and of the temperature of the gas G within the rotary kiln 10 over the length L of the rotary kiln 10, in particular its vessel 10V.

10 The temperature of the material M increases from the material inlet temperature T_{M1} towards the material heating temperature T_{M2} whereas the temperature of the gas G decreases from the gas inlet temperature T_{G1} to the gas outlet temperature T_{G2} .

15 Preferably, the material heating temperature T_{M2} , i.e. the maximum temperature of the material M, within the rotary kiln 10 is 1 100 °C or 1 050 °C. In this way, sintering/partial melting of the material M can be prevented and ZnO can be nearly fully recovered while maintaining high production rates.

The material heating temperature T_{M2} is preferably measured by means of a thermographic camera, such as an infrared camera.

20

The gas outlet temperature T_{G2} at the gas outlet 10X is preferably lower than 600 °C, 500 °C or 400 °C, in particular lower than 300 °C or 250 °C. In this way, the energy losses into the off-gas treatment system 40 are minimized and/or a significant amount of energy input into the rotary kiln 10 is used for treatment of the raw material M1.

25

The gas outlet temperature T_{G2} is preferably measured by means of a temperature sensor, such as a thermocouple.

30 The inflow rate V_{G1} of the process gas G1 is preferably greater than 1 500 Nm³/h per ton/h of raw material M1 and/or lower than 20 000 Nm³/h per ton/h of raw material M1, in particular between 2 000 Nm³/h per ton/h of raw material M1 and 10 000 Nm³/h per ton/h of raw material M1.

35 The inflow rate V_{G1} is preferably measured by means of a mass flow meter or an ultrasonic flow meter.

The velocity of the process gas G1 is preferably greater than 1 m/s and/or less than 6 m/s, preferably between 2 m/s and 4 m/s. If the gas velocity falls below a critical value, in particular below 1 m/s, partial adhesion of finely dispersed ZnO particles within the rotary kiln 10 occurs. Thus, the critical lower limit is necessary to ensure
5 that the ZnO particles are blown out of the rotary kiln 10. However, if the gas velocity is above a critical value, in particular 6 m/s, the process gas G1 will not sufficiently cool down.

The feed rate m_{M1} of the raw material M1 is preferably greater than 500 kg/h and/or
10 lower than 25 000 kg/h, in particular between 10 000 kg/h and 20 000 kg/h.

The feed rate m_{M1} is preferably measured/calculated by means of a dosing system, preferably wherein the dosing system is integrated in the charging hopper 50H.

15 Due to the extraction of ZnO particles, the output rate m_{M2} of the output material M2 is lower than the feed rate m_{M1} of the raw material M1. The output rate m_{M2} of the output material M2 is preferably less than 50 % or 40 %, mostly preferred less than 30 %, of the feed rate m_{M1} of the raw material M1.

20 The output rate m_{M2} of the output material M2 is preferably greater than 300 kg/ton of raw material M1 and/or lower than 800 kg/ton of raw material M1, in particular between 400 kg/ton of raw material M1 and 600 kg/ton of raw material M1.

For security reasons, in particular to avoid explosions within the plant 1 and/or to
25 increase the energy input, the (static) pressure within the rotary kiln 10 is preferably greater than the atmospheric pressure, i.e. the pressure of the surroundings, and/or greater than 101 kPa, in particular 110 kPa, and/or lower than 200 kPa or 150 kPa, mostly preferred between 115 kPa and 140 kPa. The excess pressure (compared to the atmospheric pressure) is preferably at least 5 kPa or 20 kPa and/or at most 100
30 kPa or 50 kPa.

The retention/dwell time of the raw material M1, i.e. the average time a particle of the raw material M1 travels through the rotary kiln 10, is preferably greater than 2 h or 3 h and/or less than 10 h or 8 h, in particular between 4 h and 6 h.

35 The retention/dwell time of the process gas G1, i.e. the average time a particle of the process gas G1 travels through the rotary kiln 10, is preferably greater than 4 s, 5 s,

6 s, 10 s or 15 s and/or less than 100 s or 50 s, in particular between 30 s and 90 s. A reduction in dwell time of less than 5 s, in particular of less than 4 s, negatively impacts gas utilization and reoxidation efficiency.

- 5 Fig. 3 shows in a schematic diagram the basic chemical reactions taking place within the rotary kiln 10, in particular its vessel 10V.

As already mentioned, the raw material M1 moves from the charging end towards the discharge end, in Fig. 3 from left to right, whereas the process gas G1 moves
10 from the discharge end towards the charging end, in Fig. 3 from right to left.

The raw material M1 undergoes several reduction steps. After entering the rotary kiln 10, the raw material M1 is dried and preheated through the counter-flow of the hot process gas G1. At lower temperatures, i.e. temperatures between 400 °C and
15 900 °C, iron oxide reduction steps take place, wherein iron oxide reacts with H₂ to reduced iron oxide / iron, hereinafter referred to as Fe, and water vapor H₂O(g). In this way, Fe₂O₃ is reduced gradually to Fe.

In the later stage of the reduction, i.e. when the temperature of the raw material M1
20 is high enough and/or higher than 900 °C, ZnO reduction occurs.

ZnO contained in the raw material M1 is reduced by means of H₂ to gaseous Zn(g) and H₂O(g), in particular at the solid-gas phase boundary and/or in the reduction/hot-
25 ter section SR of the rotary kiln 10.

The reduction section SR of the rotary kiln 10 is preferably located within the second half, in particular in the final third of the rotary kiln 10, beginning with the charging end thereof.

30 As illustrated in Fig. 3, the gaseous Zn(g) enters the hot gas phase and is transported by means of the gas stream towards the charging end, in Fig. 3 from right to left. As the gas temperature decreases and the water vapor concentration increases, the thermodynamic equilibrium is shifted towards ZnO(s).

35 In a reoxidation/colder section SO of the rotary kiln 10 Zn(g) reoxidizes with water vapor to ZnO(s) and recovers H₂ that was consumed during the reduction of ZnO in the raw material M1 and/or in the reduction zone SR.

The reoxidation/colder section SO of the rotary kiln 10 is preferably located within the first half of the rotary kiln 10, beginning with the charging end thereof.

5 Preferably, the water vapor used for the recovery of H_2 in the rotary kiln 10 is obtained solely through the reduction process within the rotary kiln 10, i.e., no additional water is added to the process, in particular the rotary kiln 10. However, the (premixed) process gas G1 might already contain water vapor, e.g., of less than 10 vol.-% or 20 vol.-%.

10

As already mentioned, the rotary kiln 10, in particular the vessel 10V, preferably comprises a length of at least 30 meters or 40 meters and/or of at most 120 meters, 100 meters or 80 meters. The lower limit ensures that sufficient reoxidation of the metal oxides, for example via the reaction $Zn(g) + H_2O(g) \rightarrow ZnO(s) + H_2(g)$, occurs
15 within the rotary kiln 10, leading to the recovery of both process heat and H_2 from said reoxidation. This increases the overall process efficiency such that the method can be implemented/exploited on an industrial scale. Conversely, a length of less than 30 meters will prevent sufficient reoxidation within the rotary kiln 10, resulting in low recovery of both heat and H_2 , a high gas outlet temperature TG_2 , e.g., of more
20 than 500 °C (due to insufficient heat recovery), and, thus, a significant loss of overall process efficiency.

The exothermic reoxidation of $Zn(g)$ recovers both H_2 and heat, reason why the temperature difference between the gas G and the material M in the reoxidation zone SO is lower compared to the temperature difference in the reduction zone SR, as
25 illustrated in Fig. 2.

The recovered H_2 is also used to reduce iron oxide within the raw material M1, as already explained.

30

Fig. 4 shows in a schematic diagram the changes of the main components in the gaseous phase in [vol.-%] over the length L of the rotary kiln 10.

Starting from the discharge end towards the charging end of the rotary kiln 10, in
35 Fig. 4 from right to left, the concentration of H_2 decreases whereas the concentration of $H_2O(g)$ increases. Due to the reduction process, gaseous $Zn(g)$ enters the hot gas phase at the end of the rotary kiln 10, i.e. in the reduction zone SR.

Fig. 5 shows in a schematic diagram the changes of the composition in [wt.-%] of the raw/bulk material M over the length L of the rotary kiln 10.

5 As illustrated, the concentration of iron oxides, i.e. of Fe_2O_3 , Fe_3O_4 and FeO , are reduced subsequently, wherein the transition between the various reduction reactions is continuous.

10 Due to the reduction of ZnO , the concentration of ZnO(s) in the raw/bulk material M is reduced over the length L of the rotary kiln 10, preferably to less than 5 wt.-% or 2 wt.-%. The concentration of Fe increases over the length L of the rotary kiln 10, preferably to more than 80 wt.-% or 90 wt.-%.

15 Thus, the output material M2 obtained in this way comprises a metallization degree of at least 80 wt.-% or 90 wt.-% and the concentration of ZnO is less than 5 wt.-% or 2 wt.-%, preferably less than 1 wt.-% or 0,5 wt.-%. This is the reason why the output material M2 obtained can be (directly) recycled back to EAF as common DRI.

20 To reduce the reoxidization of the Fe within the output material M2, the output material M2 can be directly treated on-site, i.e. within the plant 1. In particular, the output material M2 can be conveyed towards the briquetting apparatus 70B in which the output material is briquetted to reduce the specific surface thereof. Alternatively, the output material M2 can be melted on-site.

25 The process gas G1 loaded with the ZnO(s) particles is emitted as off-gas G2 through the gas outlet 10X. As already mentioned, heavy particles are preferably separated directly within the charging housing 10T from the off-gas G2 and optionally fed to the rotary kiln 10 again.

30 The off-gas G2 is then transported by means of the off-gas compressor/fan 40V for post treatment, in particular to the cooling apparatus 40T and/or to the filter apparatus 40F.

35 Thus, in a further method step the off-gas G2 is washed/filtered, in particular to separate the ZnO particles from the off-gas G2.

The filtered/treated ZnO particles are preferably discharged in a gas-tight manner, in particular by means of the airlock 40R, and can then be (directly) reused, e.g. for galvanization processes.

- 5 The cooled and washed/filtered off-gas G2 is then preferably dehumidified, e.g. by means of the condenser 40C, wherein water is extracted.

10 The dehumidified off-gas G2 preferably contains more than 80 vol.-%, in particular more than 90 vol.-% or 99 vol.-%, H₂ and can be directly recirculated back to the heating system 30 and/or the gas storage 20A by means of the treated gas compressor/fan 40G, as already explained.

15 However, the off-gas G2 might also be directed to the treatment unit 40S (when necessary) by means of the exhaust 40X, in particular for further treatment, e.g. for carbon capture. Alternatively, the off-gas G2 can be discharged into the environment, e.g. via a chimney.

20 Over the time, the concentration of contaminants/impurities, in particular CO, CO₂, and/or SO₂, in the off-gas G2 can increase.

25 According to a preferred method variant, the off-gas G2 is directed and/or removed from the process depending on the concentration, in particular volume fraction, of the contaminants/impurities, such as CO, CO₂ and/or SO₂, in the off-gas G2 and/or when necessary and/or when the concentration, in particular volume fraction, of the contaminants/impurities, such as CO, CO₂ and/or SO₂, in the off-gas G2 reaches or exceeds a predefined limit value, in particular of 1 vol.-%, 5 vol.-% or 10 vol.-%.

30 In this case, the off-gas G2 can be discharged via the exhaust 40X and/or directed to the treatment unit 40S and the contaminants, in particular carbon, within the off-gas G2 can be captured / filtered out, i.e. by means of adsorption, carbon scrubbing and/or membrane gas separation.

35 The filtered off-gas G2 comprising a reduced concentration, in particular volume fraction, of the contaminants, e.g. of less than 1 vol.-%, might then be recirculated back to the heating system 30 and/or the gas storage 20A, as already explained.

When the concentration, in particular volume fraction, of the contaminants, such as CO, CO₂ and/or SO₂, in the off-gas G2 reaches or falls below a predefined (second) limit value, in particular of 2 vol.-% or 1 vol.-%, the exhaust 40X is preferably deactivated and/or switched such that the off-gas G2 bypasses the treatment unit 40S.

5

With other words: The concentration of contaminants, in particular CO, CO₂ and SO₂, in the off-gas G2 exiting the rotary kiln 10 is preferably regulated, wherein the off-gas G2 is directed to the treatment unit 40S to capture at least part of the contaminants (when necessary), mostly preferred depending on the concentration of the contaminants in the off-gas G2.

10

The treated raw material M1 is preferably collected as (hot) output material M2 within the discharge housing 10H.

15

The output material M2 is then discharged in a gas-tight manner via the material outlet 10M and/or the airlock 70R.

Subsequently, the output material M2 is conveyed to a bunker and/or for interim storage, preferably by means of the conveyor 70C. Optionally, the output material M2 is briquetted prior storage, as already mentioned.

20

Due to the reoxidation, i.e., the recovery of H₂, within the rotary kiln 10, the off-gas G2 exiting the rotary kiln 10 preferably comprises more than 40 vol.-%, 50 vol.-% or 60 vol.-%, mostly preferred more than 70 vol.-% or 80 vol.-%, H₂ and/or less than 60 vol.-%, 50 vol.-% or 40 vol.-%, mostly preferred less than 30 vol.-% or 20 vol.-%, H₂O(g).

25

Thus, the difference between the percent of volume of H₂ in the process gas G1 entering the rotary kiln 10 and the percent of volume of H₂ in the off-gas G2 exiting the rotary kiln 10 is preferably less than 60 vol.-% or 50 vol.-%, mostly preferred less than 40 vol.-%, 30 vol.-% or 20 vol.-%.

30

If no sufficient reoxidation within the rotary kiln 10 takes place, e.g., by using a length for the rotary kiln 10 of less 30 meters, the off-gas G2 would contain less (recovered) H₂, e.g., of less than 40 vol.-%, and more H₂O(g), e.g., of more than 60 vol.-%, resulting in a significant loss of overall process efficiency. Further, the off-gas G2 would

35

carry (condensed) metallic Zn (liquid or solid), i.e., non-oxidized Zn, that would require complex methods for recovery.

5 Further aspects of the present invention, that can be realized independently or in any combination, are listed in the following:

1. Method for recycling metal oxides, in particular zinc oxides (ZnO), from a raw material (M1), in particular flue dusts, sludges, scales, iron ore and/or filter cakes, by means of a rotary kiln (10), comprising the steps:

- 10
- feeding the raw material (M1) into a charging end of the rotary kiln (10),
 - heating a process gas (G1) comprising hydrogen (H₂) to a gas inlet temperature (T_{G1}),
 - 15 - introducing the process gas (G1) into a discharge end of the rotary kiln (10),
 - heating the raw material (M1) by means of the heated process gas (G1),
 - 20 - reducing metal oxides of the raw material (M1) by means of the hydrogen (H₂) to gaseous metal and water vapor (H₂O) in a hotter/reduction section (SR) of the rotary kiln (10),
 - recovering hydrogen (H₂) and producing heat by reoxidizing the gaseous metal with water vapor (H₂O) to hydrogen (H₂) and metal oxide particles in a colder/reoxidation section (SO) of the rotary kiln (10), and
 - 25 - emitting the process gas (G1) as off-gas (G2) containing the recovered hydrogen (H₂) and the reoxidized metal oxide particles through a gas outlet (10X) of the rotary kiln (10).
- 30

2. Method according to aspect 1, wherein the rotary kiln (10) is operated in a counter-current manner, the raw material (M1) being fed from the charging end towards the discharge end into a first direction (D1) and the process gas (G1) flowing from the discharge end towards the charging end into a second direction (D2) that is opposite to the first direction (D1).

35

3. Method according to aspect 1 or 2, wherein the process gas (G1) is heated by means of a plasma torch (30T) and/or by partial combustion of hydrogen (H₂) in the process gas (G1), in particular of more than 1 vol.-% and/or less than 10 vol.-% of

40

the hydrogen (H_2) in the process gas (G1), preferably wherein the process gas (G1) is heated prior entering the rotary kiln (10).

4. Method according to any of the preceding aspects, wherein the maximum temperature (T_{M2}) of the raw material (M1) within the rotary kiln (10) is 1 100 °C, preferably 1 050 °C.
5. Method according to any of the preceding aspects, wherein the feed rate (m_{M1}) of the raw material (M1) is greater than 500 kg/h and/or lower than 20 000 kg/h and/or wherein the inflow rate (V_{G1}) of the process gas (G1) is greater than 1 500 Nm³/h per ton/h of raw material (M1) and/or lower than 20 000 Nm³/h per ton/h of raw material (M1), in particular between 2 000 and 10 000 Nm³/h per ton/h of raw material (M1).
6. Method according to any of the preceding aspects, wherein the gas inlet temperature (T_{G1}) of the process gas (G1) is greater than 1, 100 °C or 1 200 °C and/or wherein the gas outlet temperature (T_{G2}) of the off-gas (G2) at the gas outlet (10X) is lower than 400 °C, in particular 300 °C, and/or greater than 100 °C.
7. Method according to any of the preceding aspects, wherein the off-gas composition, in particular the volume fraction of hydrogen (H_2) and of water (H_2O) in the off-gas (G2), is determined, preferably to calculate the consumption of hydrogen (H_2), wherein the inflow rate (V_{G1}) and/or the gas inlet temperature (T_{G1}) are/is adjusted depending on the determined off-gas composition.
8. Method according to any of the preceding aspects, wherein the off-gas (G2) exiting the rotary kiln (10) is cooled in a cooling apparatus (40T), filtered and/or washed in a filter apparatus (40F) to separate the metal oxide particles from the off-gas (G2) and/or from water vapor (H_2O) and/or dehumidified in a condenser (40C).
9. Method according to any of the preceding aspects, wherein the concentration of contaminants, in particular carbon monoxide (CO), carbon dioxide (CO₂) and/or sulphur dioxide (SO₂), in the off-gas (G2) exiting the rotary kiln (10) is regulated, preferably wherein the off-gas (G2) is – when necessary – directed to a treatment unit (40S) to capture at least part of the contaminants, mostly preferred depending on the concentration of the contaminants in the off-gas (G2).

10. Method according to any of the preceding aspects, wherein the treated, in particular cooled, filtered, washed and/or dehumidified, off-gas (G2) is recirculated to the rotary kiln (10), in particular via a heating system (30).

5 11. Method according to any of the preceding aspects, further comprising the step of discharging the treated raw material (M1) as output material (M2) via the discharge end of the rotary kiln (10), wherein at least a part of the process gas (G1) is directed through the output material (M2) to preheat the process gas (G1) and/or to cool the output material (M2).

10 12. Plant (1) for recycling metal oxides, in particular zinc oxides (ZnO), from a raw material (M1), in particular flue dusts, sludges, scales, iron ore and/or filter cakes, the plant (1) comprising:

- 15
- a rotary kiln (10),
 - a gas supply system (20) to supply a process gas (G1) with hydrogen (H₂),
 - 20 - a heating system (30) to heat the process gas (G1), and
 - an off-gas treatment (40) system to treat off-gas (G2) exiting the rotary kiln (10) and to recirculate the treated off-gas (G2) back to the heating system (30),
- 25

wherein the plant (1) is adapted to carry out the method according to one of the preceding aspects.

30 13. Plant according to aspect 12, wherein the heating system (30) comprises at least one preferably non-transferred DC plasma torch (30T).

14. Plant according to aspect 12 or 13, wherein the off-gas treatment system (40) comprises a treatment unit (40S) to capture contaminants, in particular carbon monoxide (CO), carbon dioxide (CO₂) and/or sulphur dioxide (SO₂), in the off-gas (G2).

35 15. Plant according to any of aspects 12 to 14, wherein the rotary kiln (10) is sealed off from its surroundings.

Individual aspects, features and method steps of the present invention can be realized independently, but also in any combination and/or sequence.

List of reference signs:

1	plant	60	control system
10	rotary kiln	60C	control unit
10A	airlock	60M	first measuring device
10B	bear ring	60N	second measuring device
10D	drive	60F	third measuring device
10E	gas inlet	60G	fourth measuring device
10F	basis		
10H	discharge housing/hood	70	material output system
10M	material outlet	70B	briquetting apparatus
10N	dust outlet	70C	material conveyor
10S1	first seal	70R	airlock
10S2	second seal		
10T	charging housing/hood	CO	carbon monoxide
10V	vessel	CO ₂	carbon dioxide
10X	gas outlet	D1	first direction
		D2	second direction
20	gas supply system	Fe	iron
20A	first gas storage	FeO	iron(II) oxide
20B	second gas storage	Fe ₂ O ₃	iron(III) oxide
20C	first compressor/fan	Fe ₃ O ₄	iron(II, III) oxide
20D	second compressor/fan	G1	process gas
20M	mixing device	G2	off-gas
		H ₂	hydrogen
30	heating system	H ₂ O(g)	water vapor
30C	combustion chamber	H ₂ O(l)	liquid water
30H	heat exchanger	L	length of rotary kiln
30T	plasma torch	M1	raw material
		M2	output material
40	off-gas treatment system	m _{M1}	feed rate of raw material
40C	condenser	m _{M2}	output rate of output material
40F	filter apparatus	N ₂	nitrogen
40G	treated gas compressor/fan	R	rotation axis
40P	product conveyor	SO	reoxidation section
40R	airlock	SR	reduction section
40S	treatment unit	T	temperature
40T	cooling apparatus	T _{G1}	gas inlet temperature
40V	off-gas compressor/fan	T _{G2}	gas outlet temperature
40W	pump	T _{M1}	raw material temperature
40X	exhaust	T _{M2}	material heating temperature
		V _{G1}	inflow rate
50	raw material supply system	V _{G2}	outflow rate
50F	feeding apparatus	Zn	zinc
50H	charging hopper	ZnO	zinc oxide
50P	inlet chute		
50R	airlock		

Claims:

1. Method for recycling metal oxides, namely zinc oxides (ZnO), from a raw material (M1), in particular flue dusts, sludges, scales, iron ore and/or filter cakes, by means of a rotary kiln (10) having a length of at least 30 meters and being operated in a counter-current manner, comprising the steps:
 - feeding the raw material (M1) into a charging end of the rotary kiln (10),
 - heating a process gas (G1) comprising hydrogen (H₂) to a gas inlet temperature (T_{G1}) greater than 1100 °C,
 - introducing the process gas (G1) into a discharge end of the rotary kiln (10),
 - heating the raw material (M1) by means of the heated process gas (G1),
 - reducing metal oxides of the raw material (M1) by means of the hydrogen (H₂) to gaseous metal and water vapor (H₂O) in a hotter/reduction section (SR) of the rotary kiln (10),
 - recovering hydrogen (H₂) and producing heat by reoxidizing the gaseous metal with water vapor (H₂O) to hydrogen (H₂) and metal oxide particles in a colder/reoxidation section (SO) of the rotary kiln (10), and
 - emitting the process gas (G1) as off-gas (G2) containing the recovered hydrogen (H₂) and the reoxidized metal oxide particles through a gas outlet (10X) of the rotary kiln (10).
2. Method according to claim 1, wherein the process gas (G1) comprises more than 50 vol.-% or 70 vol.-%, preferably more than 90 vol.-% or 95 vol.-%, hydrogen (H₂) and/or less than 50 vol.-% or 30 vol.-%, preferably less than 10 vol.-% or 5 vol.-%, water vapor (H₂O).
3. Method according to claim 1 or 2, wherein the process gas (G1) is fed towards a heating system (30) to heat the process gas (G1) to the gas inlet temperature (T_{G1}).
4. Method according to any of the preceding claims, wherein the static pressure within the rotary kiln (10) is greater than the atmospheric pressure, in particular greater than 101 kPa or 110 kPa and/or lower than 200 kPa or 150 kPa.

5. Method according to any of the preceding claims, wherein the feed rate (m_{M1}) of the raw material (M1) is greater than 500 kg/h and/or lower than 25 000 kg/h, preferably between 10 000 kg/h and 20 000 kg/h.
- 5 6. Method according to any of the preceding claims, wherein the inflow rate (V_{G1}) of the process gas (G1) is greater than 1 500 Nm³/h per ton/h of raw material (M1) and/or lower than 20 000 Nm³/h per ton/h of raw material (M1), in particular between 2 000 and 10 000 Nm³/h per ton/h of raw material (M1).
- 10 7. Method according to any of the preceding claims, wherein the gas inlet temperature (T_{G1}) of the process gas (G1) is greater than 1 200 °C.
8. Method according to any of the preceding claims, wherein the gas outlet temperature (T_{G2}) of the off-gas (G2) at the gas outlet (10X) is lower than 600 °C, 500 °C
15 or 400 °C, in particular 300 °C, and/or greater than 100 °C.
9. Method according to any of the preceding claims, wherein the velocity of the process gas (G1) is greater than 1 m/s and/or less than 6 m/s, preferably between 2 m/s and 4 m/s.
20
10. Method according to any of the preceding claims, wherein the retention time of the raw material (M1) is greater than 2 h or 3 h and/or less than 10 h or 8 h, in particular between 4 h and 6 h.
- 25 11. Method according to any of the preceding claims, wherein the retention/dwell time of the process gas (G1) is greater than 4 s, 5 s, 10 s or 15 s and/or less than 100 s or 50 s, in particular between 30 s and 90 s.
12. Method according to any of the preceding claims, wherein the off-gas composition, in particular the volume fraction of hydrogen (H₂) and of water (H₂O) in the off-gas (G2), is determined, preferably to calculate the consumption of hydrogen (H₂),
30 wherein the inflow rate (V_{G1}) and/or the gas inlet temperature (T_{G1}) are/is adjusted depending on the determined off-gas composition.
- 35 13. Method according to any of the preceding claims, wherein the off-gas (G2) exiting the rotary kiln (10) comprises more than 40 vol.-%, 50 vol.-% or 60 vol.-%, mostly preferred more than 70 vol.-% or 80 vol.-%, hydrogen (H₂) and/or less than 60 vol.-%

%, 50 vol.-% or 40 vol.-%, mostly preferred less than 30 vol.-% or 20 vol.-%, water vapor (H₂O).

14. Method according to any of the preceding claims, wherein the off-gas (G2) exiting the rotary kiln (10) is cooled in a cooling apparatus (40T).

15. Method according to any of the preceding claims, wherein the off-gas (G2) exiting the rotary kiln (10) is filtered and/or washed in a filter apparatus (40F) to separate the metal oxide particles from the off-gas (G2) and/or from water vapor (H₂O).

16. Method according to any of the preceding claims, wherein the off-gas (G2) exiting the rotary kiln (10) is dehumidified in a condenser (40C).

17. Method according to any of the preceding claims, wherein the treated, in particular cooled, filtered, washed and/or dehumidified, off-gas (G2) is recirculated to the rotary kiln (10), in particular via a compressor/fan (40V) and/or a heating system (30).

18. Method according to any of the preceding claims, further comprising the step of discharging the treated raw material (M1) as output material (M2) via the discharge end of the rotary kiln (10), wherein at least a part of the process gas (G1) is directed through the output material (M2) to preheat the process gas (G1) and/or to cool the output material (M2).

19. Plant (1) for recycling zinc oxides (ZnO) from a raw material (M1), in particular flue dusts, sludges, scales, iron ore and/or filter cakes,

the plant (1) comprising:

- a rotary kiln (10) with a length of at least 30 meters,
- a gas supply system (20) to supply a process gas (G1) with hydrogen (H₂),
- a heating system (30) to heat the process gas (G1), and
- an off-gas treatment (40) system to treat off-gas (G2) exiting the rotary kiln (10) and to recirculate the treated off-gas (G2) back to the heating system (30),

wherein the plant (1) is adapted to carry out the method according to one of the preceding claims.

20. Plant according to claim 19, wherein the plant (1), in particular the rotary kiln (10), is sealed off from its surroundings.
21. Plant according to claim 19 or 20, wherein the plant (1) comprises a sealing
5 system operated with seal gas to seal off the plant (1), in particular the rotary kiln (10), from its surroundings, wherein the sealing system is connected to the gas supply system (30).
22. Plant according to any of claims 19 to 21, wherein the heating system (30) com-
10 prises an electrically operated heating chamber to heat the process gas (G1) to a gas inlet temperature (T_{G1}) greater than 1100 °C.
23. Plant according to any of claims 19 to 22, wherein the plant (1) comprises a
15 discharge housing (10H) forming a discharge end of the rotary kiln (10) through which the treated raw material (M1) can be discharged as output material (M2), wherein the discharge housing (10H) comprises an additional gas inlet at its lower end such that at least a part of the process gas (G1) can be directed through the output material (M2).

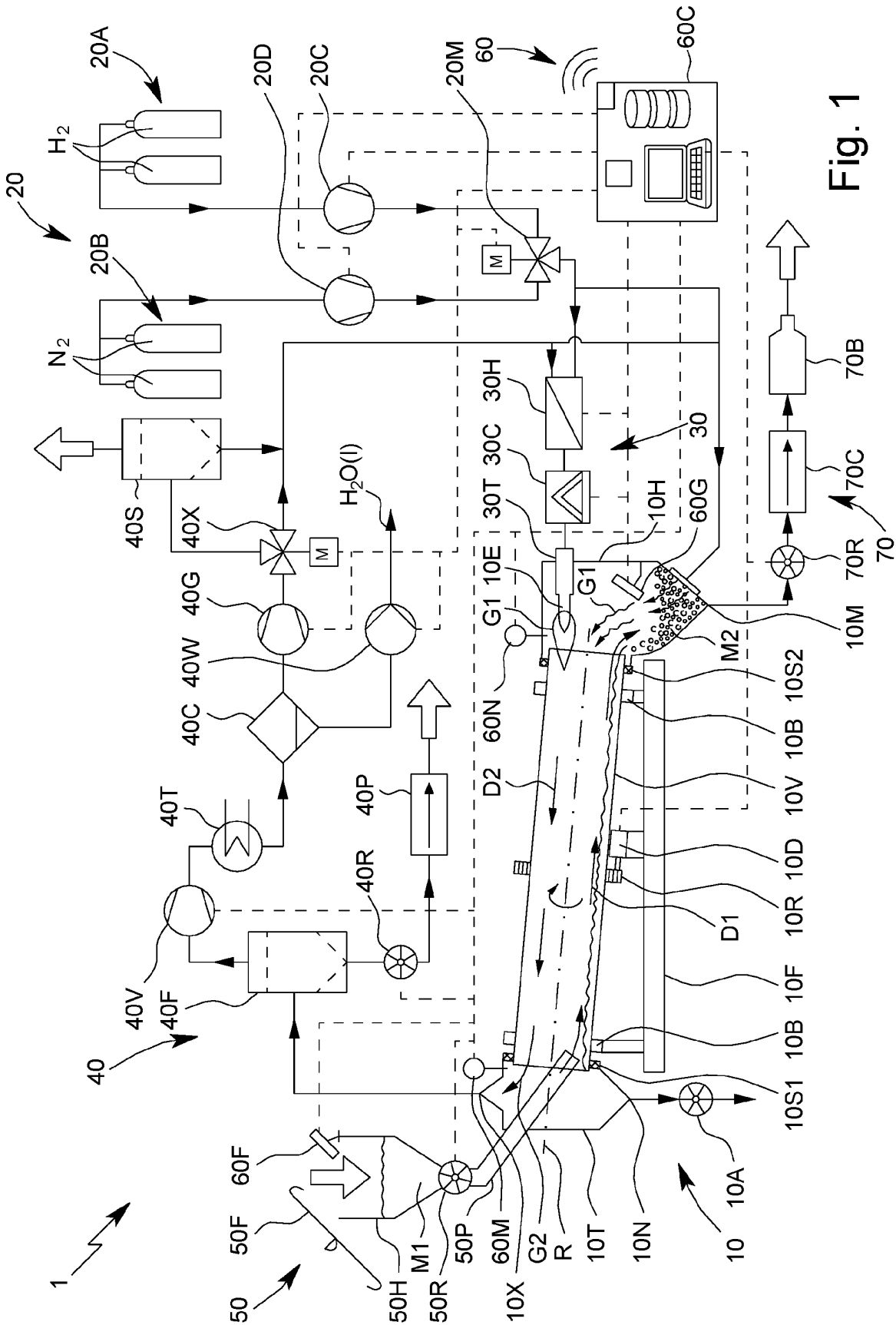


Fig. 1

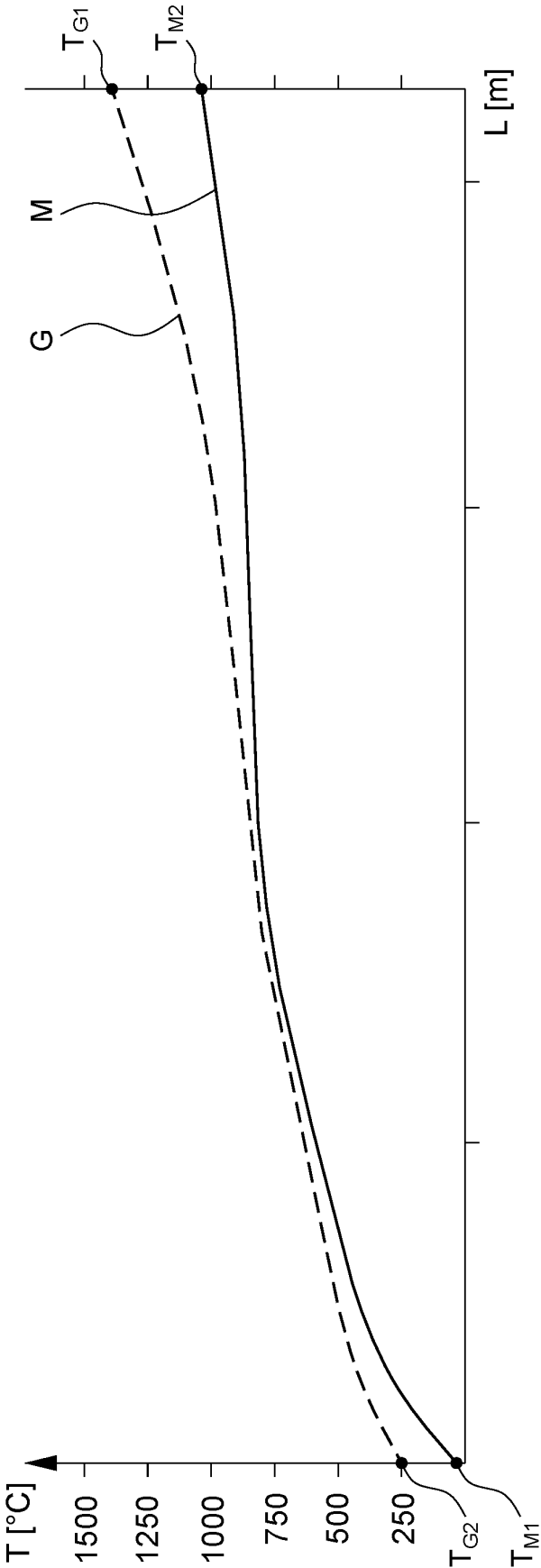


Fig. 2

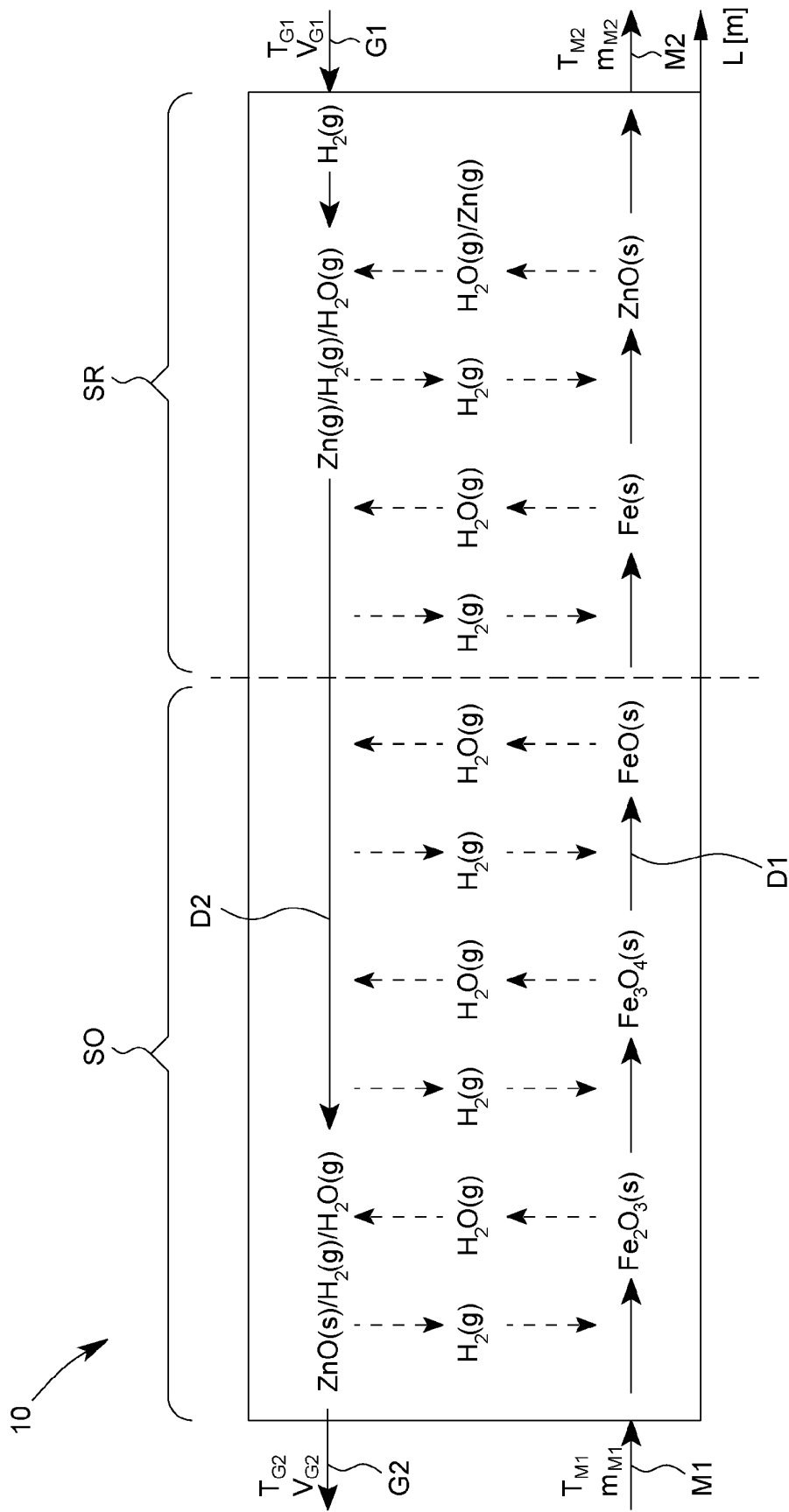


Fig. 3

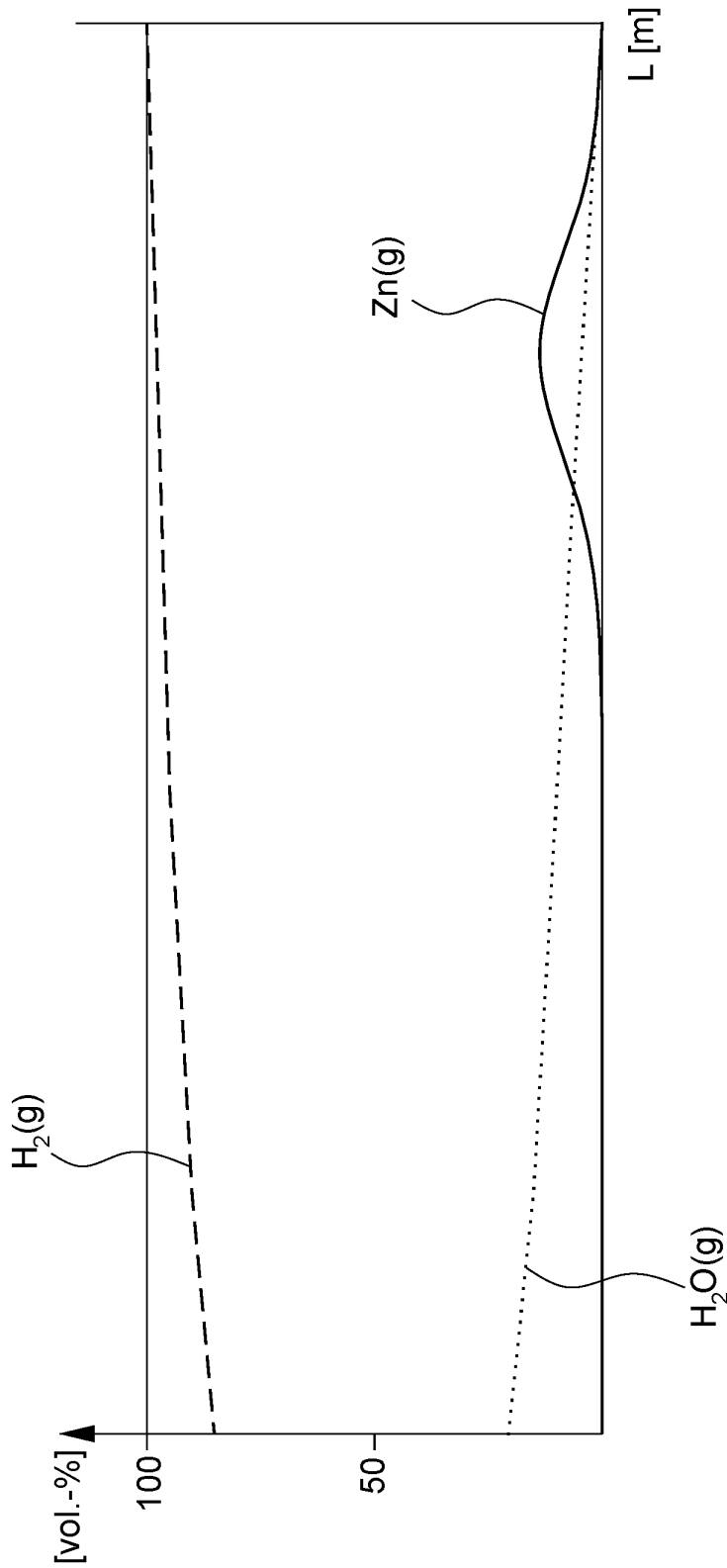


Fig. 4

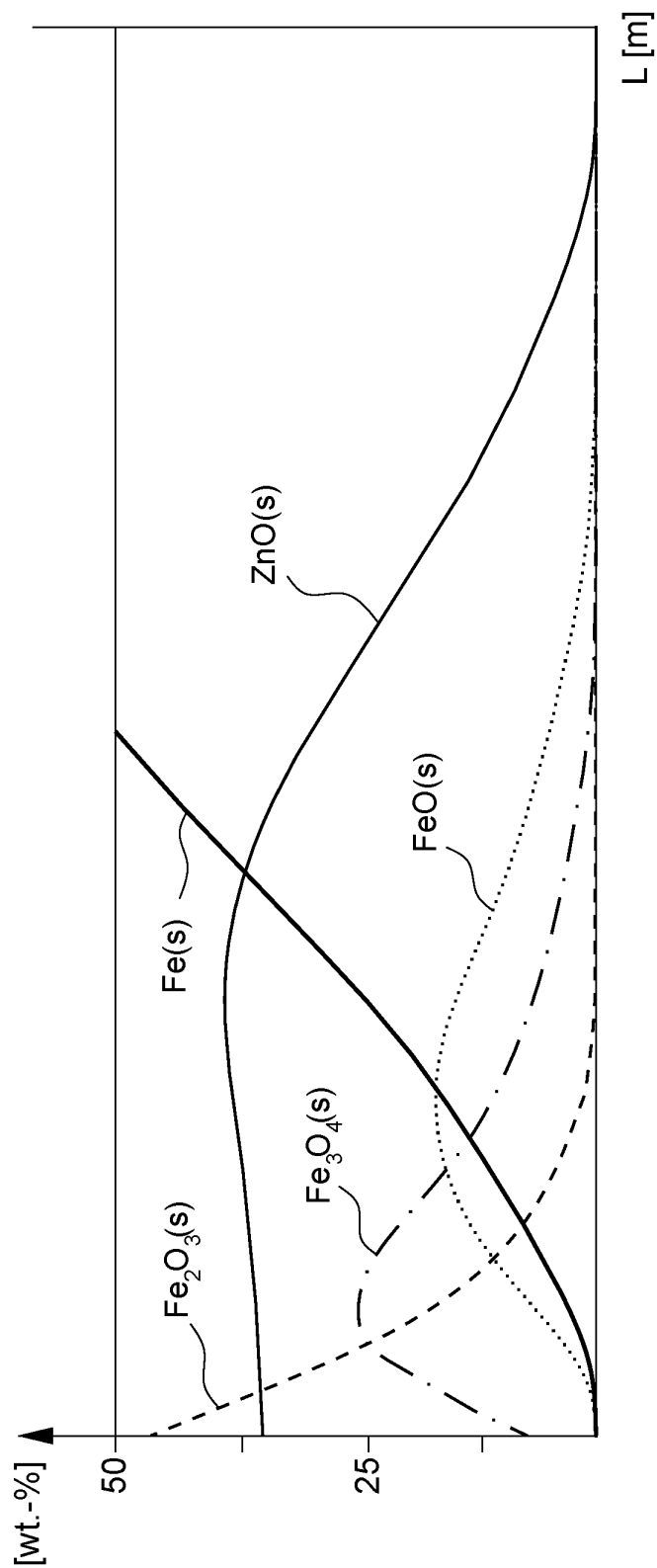


Fig. 5

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2025/060698

A. CLASSIFICATION OF SUBJECT MATTER

INV. C22B19/38 C22B4/00 C22B4/08 C22B5/12 C22B5/18
 C22B7/02 C22B7/04 C22B19/30 F27B7/34 F27B7/36
 F27D17/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C22B C21B F27D F27B

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

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

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 98/18971 A1 (AGGLO INC [CA]) 7 May 1998 (1998-05-07)	1, 3 - 6, 8 - 12, 14 - 23
A	abstract page 5, line 18 - page 6, line 15 ----- - / - -	2, 7, 13



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

30 July 2025

Date of mailing of the international search report

18/08/2025

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2

NL - 2280 HV Rijswijk

Tel. (+31-70) 340-2040,

Fax: (+31-70) 340-3016

Authorized officer

Kim Lee, Bij Na

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2025/060698

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
T	STEWART DANIEL J C ET AL: "Pyrometallurgical removal of zinc from basic oxygen steelmaking dust - A review of best available technology", RESOURCES, CONSERVATION AND RECYCLING, ELSEVIER, AMSTERDAM, NL, vol. 157, 5 March 2020 (2020-03-05), XP086146894, ISSN: 0921-3449, DOI: 10.1016/J.RESCONREC.2020.104746 [retrieved on 2020-03-05] abstract figure 8 subsection 5.1 The Waelz kiln -----	
A	EP 0 972 849 A1 (NIPPON STEEL CORP [JP]; SANYO SPECIAL STEEL CO LTD [JP]) 19 January 2000 (2000-01-19) abstract -----	1-23
A	PICHLER C ET AL: "Pyrolysis Gas as a Renewable Reducing Agent for the Recycling of Zinc- and Lead-Bearing Residues: A Status Report", JOM: JOURNAL OF METALS, SPRINGER NEW YORK LLC, UNITED STATES, vol. 69, no. 6, 13 April 2017 (2017-04-13), , pages 999-1006, XP036248953, ISSN: 1047-4838, DOI: 10.1007/S11837-017-2341-7 [retrieved on 2017-04-13] abstract -----	1-23

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2025/060698

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9818971	A1	07-05-1998	AU 4769297 A	22-05-1998
			CA 2269937 A1	07-05-1998
			US 5906671 A	25-05-1999
			WO 9818971 A1	07-05-1998

EP 0972849	A1	19-01-2000	CN 1214740 A	21-04-1999
			EP 0972849 A1	19-01-2000
			KR 19990087253 A	15-12-1999
			WO 9732048 A1	04-09-1997
