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(71) Applicant: **OUTOTEC (FINLAND) OY** [FI/FI];  
Rauhalanpuisto 9, 02230 Espoo (FI).

(72) Inventors: **KOTIRANTA, Tuukka**; Kolitie 23, 28200 Pori (FI). **PALOVAARA, Petri**; Enmustajantie 4, 28220 Pori (FI). **PISILÄ, Sauli**; Mallastie 12a 12, 90520 Oulu (FI).

(74) Agent: **KOLSTER OY AB**; (Salmisaarenaukio 1), P.O.Box 204, FI-00181 Helsinki (FI).

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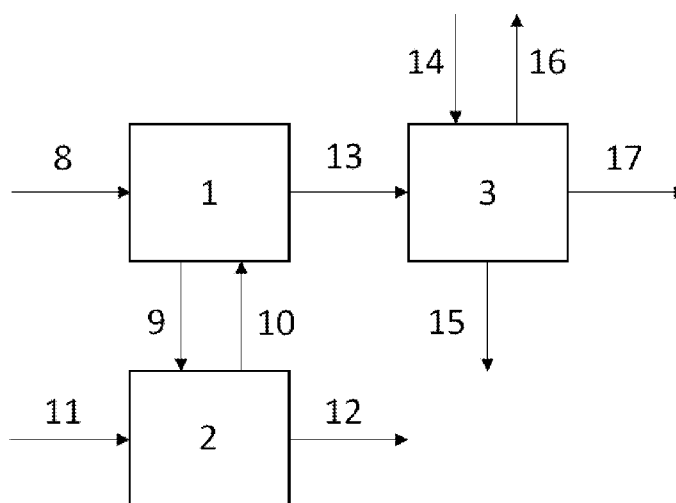
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(54) Title: RECOVERY OF METALS FROM CALCIUM-RICH MATERIALS

Figure 1



(57) Abstract: Provided herein is a process for recovering metal(s) from calcium rich iron containing material (8), comprising (a) leaching (1) calcium one or more times from said calcium rich iron containing material (8) to obtain a calcium depleted iron containing material (13); and (b) subjecting the calcium depleted iron containing material (13) to pyrometallurgical treatment (3) to recover metal(s) (17) from said calcium depleted iron containing material (13).

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## RECOVERY OF METALS FROM CALCIUM-RICH MATERIALS

### FIELD OF THE INVENTION

The present invention relates to recovery of valuable metals from calcium rich iron containing materials by pyrometallurgical treatment and more particularly to process comprising removal of calcium from the calcium rich iron containing starting material prior to the pyrometallurgical treatment.

### BACKGROUND OF THE INVENTION

Some steel plants use iron ore that contains vanadium and other residue metals. These metals and other nonferrous oxides typically end up in the slag during the steelmaking process. This slag is typically landfilled and not used as a product due to the fact that it contains the said metal oxide residues that have been proved to be harmful for the environment. The conventional way to recover these valuable metals is to subject the said slag to smelting.

During the smelting process most of the iron- and vanadium oxides (along with other trace alloying metals) are reduced to the metal phase in the presence of a reductant (typically carbon bearing anthracite, coke or metallic reductants, typically Al, FeSi or any other reducing substance). Typically the smelting vessel is an electric arc furnace (alternating current or direct current type). During the smelting process other unreduced oxides form the furnace slag, Calcium oxide in this slag makes the liquidus temperature of the slag high and as much as 24% w/w silica flux of total solid feed to the furnace may be required for melting the slag. This amount reflects a situation where the fluxing mix consists solely of quartz and calcium content of the feed material is 45% w/w calculated as CaO.

One of the disadvantages associated with the use of flux material is that impurities resulting from the flux material end up in the obtained products. In this case metal product silicon content will be higher when silica flux is used. This is due to the higher silicon oxide input into the furnace compared to the amount of formed metal, which stays roughly at the same level regardless of the used flux amount. Typically some percentage of the silicon fed to the system reports to the metal phase. Therefore when tonnage of input silicon is higher while rest of metal forming components stay the same, the metal silicon content will be higher also.

The metal phase from the smelting goes to a converting step, where vanadium and other valuable metals are selectively oxidized to the slag. The slag is further treated with salt roasting. In the salt roasting calcium further forms insoluble salts, in particular with vanadium, which causes losses in the following hydrometallurgical treatment stages if calcium is not removed to the sufficient level in the previous processing steps.

#### BRIEF DESCRIPTION OF THE INVENTION

An object of the present invention is thus to provide a process for recovery of valuable metal(s) from calcium rich iron containing materials so as to overcome the above problems. The objects of the invention are achieved by processes which are characterized by what is stated in the independent claims. The preferred embodiments of the invention are disclosed in the dependent claims.

The invention is based on the surprising realization that removal of calcium from calcium rich iron containing starting material prior to pyrometallurgical treatment by leaching allows more efficient pyrometallurgical treatment. Removal of calcium from the material lowers the liquidus temperature of the material in smelting and thus lowers the required amount of flux material or even makes use of flux material redundant. As a result the smelting phase feed amount, residual slag amount and energy consumption are significantly lower. Removal of calcium may also improve the quality of the products obtained from the pyrometallurgical treatment.

This invention can also be utilized to a processing option of feeding the starting material after removal of calcium straight to roasting without the previously explained smelting and converting steps. It is possible to reach such a low levels of calcium after the removal of calcium to avoid excessive formation of insoluble calcium salts in the roasting.

Another benefit of the present process is that calcium removal step removes hydroxides and carbonates bound in calcium such as  $\text{Ca(OH)}_2$  and  $\text{CaCO}_3$ . This lowers furnace energy and reductant consumption and makes gas handling and pressure control of the furnace easier and therefore safer. In the conventional smelting process if the slag is stored outside pre-drying under  $200^\circ\text{C}$  only removes free water and some of crystal waters and all hydroxides and carbonates are left to the furnace feed.

## BRIEF DESCRIPTION OF THE DRAWINGS

In the following the invention will be described in greater detail by means of preferred embodiments with reference to the attached drawings, in which

- 5           Figure 1 shows a first example of the present process;  
            Figure 2 shows a second example of the present process;  
            Figure 3 shows a third example of the present process; and  
            Figure 4 shows a fourth example of the present process.

## DETAILED DESCRIPTION OF THE INVENTION

10           Provided herein is a process for recovery of metal(s) from a calcium rich iron containing material, comprising

            (a) leaching calcium one or more times from said calcium rich iron containing material to obtain a calcium depleted iron containing material; and

            (b) subjecting the calcium depleted iron containing material to pyro-  
15           metallurgical treatment to recover metal(s) from said calcium depleted iron containing material.

            The term "calcium rich iron containing material" refers to materials comprising calcium, iron and optionally other valuable metal(s). Said other valuable metals are typically at least vanadium. Typically the calcium rich iron containing material comprises at least 20% w/w, in particular at least 25% w/w, more particularly at least 30% w/w, even more particularly at least 40% w/w, calcium. Calcium is typically present as CaO, Ca(OH)<sub>2</sub>, CaCO<sub>3</sub>, calcium silicates and/or other calcium containing compounds. Typically the calcium rich iron containing material comprises at least 5% w/w, in particular at least 10% w/w, more  
20           particularly at least 15% w/w, iron. In particular the calcium rich iron containing material comprises from 5 to 60% w/w iron. Iron is typically present as Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>2</sub>O<sub>3</sub>, FeO, metallic Fe and/or iron silicates.

            In particular the calcium rich iron containing material further comprises vanadium, typically at least 0.2% w/w, in particular at least 0.5% w/w, more particular at least 1% w/w, even more particularly at least 1.5% w/w. Vanadium is typically present as vanadium oxide(s), in particular V<sub>2</sub>O<sub>5</sub>.  
30

            A typical example of a calcium rich iron containing material suitable to be treated by the present process is slag, such as steel converter slag or steel making slag. A particular example of said calcium rich iron containing material is LD slag, also known as basic oxygen furnace slag (BOS) or LD-converter slag, a by-  
35

product of the Linz-Donawitz process where pig iron is processed into crude steel.

A particular example of the present process is a process for recovering iron and vanadium from LD slag, comprising

- 5 (o) providing LD slag;  
(i) leaching calcium one or more times from said LD slag to obtain calcium depleted LD slag; and  
(ii) subjecting the calcium depleted LD slag to pyrometallurgical treatment to recover iron and vanadium from the calcium depleted LD slag.

10 The term "comprise" as used herein and hereafter describes the referred items in a non-limiting manner, e.g. the present processes comprising defined process stages consist, at least, of the said stages, but may additionally, when desired, comprise other process stages. However, the processes comprising defined process stages may consist of only the said process stages.

15 In accordance with the present process the present calcium rich iron containing material is subjected to (a) leaching to remove calcium from the material prior to (b) pyrometallurgical treatment(s).

Figure 1 shows a first example of the present process wherein calcium rich iron containing material 8 is fed to a calcium removal stage 1, wherein the calcium removal is accomplished by leaching in a (calcium poor) leaching solution 10 to obtain a calcium depleted material 13 and calcium rich leaching solution 9. The thus obtained calcium depleted iron containing material 13 is then fed to a pyrometallurgical treatment stage, which in this example is a smelting stage 3 performed under an elevated temperature and reducing conditions and in the presence of a flux material 14 to obtain hot metal 17 which comprises the desired valuable metals, slag 15 and evaporated material 16. The calcium rich leaching solution 9 obtained from the calcium removal stage 1 is subjected to calcium precipitation 2 by feeding a carbon dioxide containing gas 11 into the calcium rich leaching solution to precipitate calcium carbonate ( $\text{CaCO}_3$ ) 12 and to obtain a calcium poor leaching solution 10 which is then recirculated back to the calcium removal stage 1.

Figure 2 shows a second example of the present process. In the process illustrated in Figure 2 a calcium rich iron containing material 8 is subjected to a calcium removal stage 1 accomplished by leaching in a (calcium poor) leaching solution 10 to obtain a calcium depleted iron containing material 13 and calcium rich leaching solution 9. The thus obtained calcium depleted iron containing

material 13 is then fed to a pyrometallurgical treatment stage, which in this example is a roasting stage 5 performed under an elevated temperature, typically in the presence of salt(s), to obtain a roasted slag 20 which comprises the desired valuable metals. Calcium rich leaching solution 9 obtained from the calcium removal stage 1 is subjected to calcium precipitation 2 by feeding a carbon dioxide containing gas 11 into the calcium rich leaching solution to obtain calcium carbonate ( $\text{CaCO}_3$ ) 12 and a calcium poor leaching solution 10 which is recirculated to the calcium removal stage 1.

Suitable leaching solutions for removing calcium from the calcium rich iron containing material in stage (a), and similarly in stage (i), are e.g. those selected from the group consisting of acetic acid, nitric acid, propionic acid, aqueous solutions of ammonium salts, such as aqueous solution of ammonium acetate ( $\text{CH}_3\text{COONH}_4$ ), ammonium chloride ( $\text{NH}_4\text{Cl}$ ) or ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ), Preferably the present leaching solution is an aqueous salt solution, in particular an aqueous solution of an ammonium salt, more particularly an aqueous solution of ammonium acetate ( $\text{CH}_3\text{COONH}_4$ ), ammonium chloride ( $\text{NH}_4\text{Cl}$ ) or ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ), most preferably ammonium chloride ( $\text{NH}_4\text{Cl}$ ). The salt concentration of the aqueous salt solution is typically from 0.2 to 8 M, preferably 0.5 to 5 M, more preferably 0.5 to 2 M.

Leaching in the calcium removal stage (a), and similarly in stage (i), is typically performed at a temperature of from 0 to  $100^\circ\text{C}$ , preferably from 10 to  $70^\circ\text{C}$ , more preferably from 20 to  $70^\circ\text{C}$ . Most preferably, the leaching is performed at temperature of 20 to  $60^\circ\text{C}$ , using an aqueous salt solution. The desired crystal form of the precipitated calcium carbonate has an effect on the leaching temperature since different crystal forms precipitate in different temperatures and the solution is circulated. There is no need to cool down or heat the solution before leaching stage.

Leaching in the calcium removal stage (a), and similarly in stage (i), may be performed one or more times.

As calcium removal is stage (a), and similarly in stage (i), is performed to lower the calcium concentration in the feed to the pyrometallurgical treatment stage (b), and similarly to stage (ii), and in smelting some calcium is needed to lower the liquidus temperature of the slag, it is a matter of optimization whether the calcium is removed only partly in the calcium removal stage (a), and similarly in stage (i), and/or whether some calcium rich iron containing material is fed directly to the smelting without calcium removal, or whether calcium is removed as

much as possible in the calcium removal stage (a), and similarly in stage (i). Preferably at least 60% w/w of the calcium present in the calcium rich iron containing material is removed.

5 When calcium is desired to be removed only partly, it is preferred to perform a single stage leaching in stage (a), and similarly in stage (i), and preferably to remove from 60 to 90% w/w, more preferably from 65 to 85% w/w of the calcium from the calcium rich iron containing material. In this case the amount of calcium in the calcium depleted iron containing material is preferably below 25% w/w, more preferably below 20% w/w, even more preferably below 17% w/w.

10 When as much calcium as possible is desired to be removed, then leaching is preferably repeated until at least 70% w/w, more preferably from 75% to 100% w/w, even more preferably from 80% to 99% of the calcium present in the calcium rich iron containing material is removed. In this case the amount of calcium in the calcium depleted iron containing material is preferably  
15 below 20% w/w, more preferably below 15% w/w, even more preferably below 10% w/w, most preferably below 1% w/w. Typically when calcium is needed to be removed as much as possible, the calcium leaching stage (a) or (i) is performed twice. The number of leaching stages indicated herein refers to number of times of taking a fresh (calcium poor) leaching solution to the leaching stage (a), and  
20 similarly to stage (i). Accordingly the several leaching stages may also be performed as separate leaching stages wherein leaching is performed in consecutively arranged leaching vessels or in a single leaching vessel which is successively refilled with fresh (calcium poor) leaching solution.

As discussed above in context of the first and second examples, in step  
25 (a), and similarly in step (i), in addition to the calcium depleted iron containing material, a used leaching solution containing calcium dissolved from the calcium rich iron containing material is obtained. Herein and hereafter said used leaching solution is also referred to as a calcium rich leaching solution. If recovery and re-use of said used leaching solution is desired, calcium should be removed from the  
30 used leaching solution to obtain a calcium poor leaching solution. Preferably this is accomplished by precipitation.

A typical example of precipitation of the calcium from the calcium rich leaching solution is carbonation. This may be accomplished by (c) optionally first filtering the used calcium rich leaching solution to remove any residual calcium  
35 rich iron containing material from said calcium rich leaching solution; and (d) bubbling carbon dioxide containing gas, in particular carbon dioxide, into the cal-

cium rich leaching solution to precipitate calcium carbonate and thus to remove calcium from said calcium rich leaching solution to obtain a regenerated calcium poor leaching solution. Said regenerated calcium poor leaching solution may then be (e) recycled to stage (a) or (i), respectively. The carbon dioxide required in stage (d) may be obtained e.g. from flue gas or other sources. The temperature of the carbonation depends on the desired crystal form of the precipitated calcium carbonate. Different crystal forms precipitate in different temperatures, for example aragonite can be precipitated at 60°C.

After removal of calcium from the material, the calcium depleted iron containing material is subjected to a pyrometallurgical treatment stage (b) or (ii). Before feeding the calcium depleted iron containing material to the pyrometallurgical treatment stage (b) or (ii) said calcium depleted iron containing material is preferably dried.

The present pyrometallurgical treatment stage (b) or (ii) may be any one or more pyrometallurgical treatment(s) known to a skilled person and found suitable for recovering desired valuable metals from the treated calcium depleted iron containing material. Typically the pyrometallurgical treatment is at least smelting or roasting. Preferably the calcium depleted material is subjected to at least smelting.

Due to the previous calcium removal stage (a) or (i) the mass flow of the calcium depleted iron containing material to the pyrometallurgical stage (b) or (ii), respectively, is smaller as compared to untreated calcium rich iron containing material as calcium is one of the major elements in the calcium rich iron containing material. This allows reduction of furnace size and decreases the amount of needed electricity during the pyrometallurgical treatment and/or allows increase of the capacity.

Further, the liquidus temperature of a mixture of said calcium depleted iron containing material and optional desired amount of untreated calcium rich iron containing material is lower as compared to the respective untreated calcium rich iron containing material. Therefore the use of flux materials is minimized. This is relevant in particular when the material is subjected to smelting in stage (b), and similarly in stage (ii).

In cases where reaching of desired slag region requires addition of calcium containing material it may be possible to also add some untreated calcium rich iron containing material to the pyrometallurgical process stage.

In accordance with the present process flux material may be used to reach the correct slag region in the smelting stage. Preferably the amount of added flux material (being other than the original calcium rich iron containing feed material without calcium removal treatment) is less than 45% w/w, more preferably less than 15% w/w and in some cases no fluxes are needed. Possible flux materials include conventional flux materials such as those selected from the group consisting of lime, wollastonite, bauxite, quartz and olivine, as well as other material comprising SiO<sub>2</sub>, CaO, MgO, and/or Al<sub>2</sub>O<sub>3</sub>.

Furthermore, iron and/or iron pellets or any other material comprising FeO, Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>2</sub>O<sub>3</sub> and/or V<sub>2</sub>O<sub>5</sub> or other materials containing significant portion of iron and/or vanadium may be added when desired. Preferably in smelting the slag region is selected to minimize the fluxing in the smelting. The following slag regions are possible: as merwinite, mellilite, rankinite, åkermanite, fosterite, spinel, monticellite, pseudowollastonite, pyroxene, dicalciumsilicate, periclase, anorthite, cordierite, mullite and other similar regions.

When the calcium deplete iron containing material is subjected to smelting in stage (b), and similarly in stage (ii), the smelting stage may be performed under conditions known to a skilled person, i.e. under elevated temperature and reducing conditions and in the presence of optional flux material(s) as discussed above. Coke is typically used as a carbon reductant in the smelting stage; however the carbon reductant can be any other carbon bearing reductant, such as anthracite. Reductant may also be metallic reductant, use of which affects energy consumption and feed rates. The smelting may be followed by converting when so desired. The smelting and the optional converting may also be followed by roasting when so desired.

In cases where iron containing material is fed directly to a roasting process without a smelting phase, it may form insoluble vanadium bearing calcium salts if it comprises excessive amounts of calcium. To minimize the formation of such salts the calcium needs to be removed from the untreated calcium rich iron containing as much as possible in the calcium removal stage (a) or (i). When the calcium deplete iron containing material is subjected to roasting in stage (b) and similarly in stage (ii), the roasting stage may be performed under conditions known to a skilled person, i.e. under elevated temperature, typically in the presence of salt(s), to obtain a roasted slag. Salts used in the roasting stage are conventionally NaCl, Na<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>SO<sub>4</sub>.

The calcium depleted iron containing material is preferably fed into the pyrometallurgical stage (b) or (ii) as fine material. It may also be pelletized, sintered and/or pre-treated by any other suitable means known to a skilled person.

5           Figure 3 shows a third example of the present process wherein calcium rich iron containing material further comprising vanadium 8 is subjected to a calcium removal stage 1 accomplished by leaching in a (calcium poor) leaching solution 10. The obtained calcium depleted iron and vanadium containing material 13 is then subjected to a smelting stage 3 under elevated temperature and reducing conditions in the presence of flux material(s) 14 to obtain hot metal 17  
10           which comprises iron and vanadium, slag 15 and evaporated material 16. The calcium rich leaching solution 9 obtained from the calcium removal stage 1 is subjected to calcium precipitation 2 by feeding a carbon dioxide containing gas 11 into the calcium rich leaching solution to precipitate calcium carbonate (CaCO<sub>3</sub>)  
15           12 and to obtain a calcium poor leaching solution 10 which is recirculated to the calcium removal stage 1. Hot metal 17 comprising iron and vanadium obtained from smelting 3 is then subjected to converting 4 to obtain pig iron 18 and slag comprising vanadium and iron 19. The slag 19 is then subjected to roasting 5 performed under an elevated temperature, typically in the presence of salt(s), to obtain  
20           roasted slag 20 which comprises vanadium and iron and which is then further subjected to hydrometallurgical treatment 6 to obtain a stream comprising iron and vanadium 22 and rejected material 21. The stream comprising iron and vanadium 22 is then subjected to an aluminothermic reduction treatment 7 to obtain ferrovanadium 23.

25           Figure 4 shows a fourth example of the present process wherein calcium rich iron containing material further comprising vanadium 8 is subjected to a calcium removal stage 1 accomplished by leaching in a (calcium poor) leaching solution 10. The obtained calcium depleted iron and vanadium containing material 13 is then subjected to roasting 5 under elevated temperature, typically in the  
30           presence of salt(s), to obtain a roasted slag 20 which comprises iron and vanadium. Calcium rich leaching solution 9 obtained from the calcium removal stage 1 is subjected to calcium precipitation 2 by feeding a carbon dioxide containing gas 11 into the calcium rich leaching solution to precipitate calcium carbonate (CaCO<sub>3</sub>) 12 and to obtain a calcium poor leaching solution 10 which is recirculated to the  
35           calcium removal stage 1. The roasted slag 20 which comprises iron and vanadium is further subjected to hydrometallurgical treatment 6 to obtain a stream com-

prising vanadium 22 and rejected material 21. The stream comprising the desired valuable metals 22 is then subjected to aluminothermic reduction treatment 7 to obtain ferrovanadium 23.

#### EXAMPLES

5           The examples for conventional and Ca-removed material are calculated with the same assumptions. V production (V content in hot metal) is fixed to 5000 tpa. V-yield is fixed to 90%. In examples, preheating/prereduction of the feed material and the availability of the furnace are not taken into account. Temperatures of tapped hot metal, tapped slag and furnace gas are fixed. Metallurgical  
10 coke is used as a carbon reductant in the calculation. The electric and heat losses in electric furnace are not taken into account, because they depend on the selected furnace type, furnace size and operating parameters. Also in the examples it is assumed that the material is fed as a fine material into the furnace (pelletizing and sintering/hardening/induration changes the energies and mass balances).

15           The used slag regions in examples are suitable for the process and are selected to minimize the fluxing in the smelting.

          In examples 4 to 7 the main feed material to the smelting is treated with calcium removal process. In that process 90% of the calcium containing compounds is removed from the feed material. The feed material is not altered in  
20 any other way.

#### Reference example 1

          In the conventional process Ca-rich material is fed directly into the furnace with quartz and carbon reductant. The slag region is mainly wollastonite (can be also similar areas). The total feed rate into furnace is 49.8 t/h and the total  
25 need for fluxes is 12 t/h. The electric power is 48 MW (excl. losses). The energy consumption is 6724 kWh/t of hot metal. Slag/metal ratio is 4.4. The production of hot metal is 7.1 t/h and for slag is 31 t/h. The content of V and Si in hot metal is 8.1 and 10.9%, respectively.

#### Reference example 2

30           In the conventional process Ca-rich material is fed directly into the furnace with quartz, olivine and carbon reductant. The slag region is mainly merwinite (can be also similar areas). The total feed rate into furnace is 54.8 t/h and the total need for fluxes is 16.9 t/h. The electric power is 52 MW (excl. losses). The energy consumption is 6809 kWh/t of hot metal. Slag/metal ratio is 4.6. The

production of hot metal is 7.7 t/h and for slag is 35 t/h. The content of V and Si in hot metal is 7.5 and 9.6%, respectively.

### Reference example 3

In the conventional process Ca-rich material is fed directly into the furnace with quartz, olivine, bauxite and carbon reductant. The slag region is mainly spinel (can be also similar areas). The total feed rate into furnace is 72.0 t/h and the total need for fluxes is 33.0 t/h. The electric power is 67 MW (excl. losses). The energy consumption is 8367 kWh/t of hot metal (excl. losses). Slag/metal ratio is 5.8. The production of hot metal is 8.1 t/h and for slag is 47 t/h. The content of V and Si in hot metal is 7.1 and 9.0%, respectively.

### Example 4

In accordance with the present process, Ca removed material is fed directly into the furnace with Ca-rich material and carbon reductant. The slag region is mainly melilite (can be also similar areas). The total feed rate into furnace is 23.7 t/h and the total need for fluxes is 7.0 t/h, where 7.0 t/h (all of the fluxes) is the original feed material bypassing the Ca removal process. The electric power is 24 MW (excl. losses). The energy consumption is 3753 kWh/t of hot metal (excl. losses). Slag/metal ratio is 1.6. The production of hot metal is 6.5 t/h and for slag is 10 t/h. The content of V and Si in hot metal is 8.8 and 3.3%, respectively.

### Example 5

In accordance with the present process, Ca removed material is fed directly into the furnace with Ca-rich material, quartz, olivine and carbon reductant. The slag region is mainly merwinite (can be also similar areas). The total feed rate into furnace is 31.8 t/h and the total need for fluxes is 17 t/h, where 12.9 t/h is the original feed material bypassing the Ca removal process. The electric power is 30 MW (excl. losses). The energy consumption is 4489 kWh/t of hot metal (excl. losses). Slag/metal ratio is 2.3. The production of hot metal is 6.8 t/h and for slag is 16 t/h. The content of V and Si in hot metal is 8.4 and 4.7%, respectively.

### Example 6

In accordance with the present process, Ca removed material is fed directly into the furnace with dolomite, bauxite and carbon reductant. The slag region is mainly spinel (can be also similar areas). The total feed rate into furnace is 35.2 t/h and the total need for fluxes is 13.3 t/h, where 0 t/h is the original feed

material bypassing the Ca removal process. The electric power is 35 MW (excl. losses). The energy consumption is 5314 kWh/t of hot metal (excl. losses). Slag/metal ratio is 2.3. The production of hot metal is 6.5 t/h and for slag is 15 t/h. The content of V and Si in hot metal is 8.8 and 3.4 %, respectively.

#### 5 **Example 7**

In accordance with the present process, Ca removed material is fed directly into the furnace with Ca-rich material, dolomite, iron pellets/concentrate and carbon reductant. In the example the Si in hot metal is diluted to 1.0% (the feed rate of the iron bearing material is 26 t/h). The slag region is mainly merwinite (can be also similar areas). The total feed rate into furnace is 59.8 t/h and the total need for fluxes is 11.0 t/h, where 4 t/h is the original feed material bypassing the Ca removal process. The electric power is 71 MW (excl. losses). The energy consumption is 2965 kWh/t of hot metal (excl. losses). Slag/metal ratio is 0.6. The production of hot metal is 23.9 t/h and for slag is 14 t/h. The content of V and Si in hot metal is 2.4 and 1.0%, respectively.

#### **Reference example 8**

Conventional roasting of such material is done with salt roasting. The purpose of the roasting is to produce water-soluble vanadium compound. The conventional feed material comes from the smelting and converting process and contains very small amounts of calcium. Typically process requires less than 1% of free lime in the feed material. The amount of salt fed to the roasting is proportional to the vanadium content of the feed material to roasting. Salts used in the roasting are conventionally NaCl, Na<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>SO<sub>4</sub>.

The calcium containing feed material is not suitable to the conventional salt roasting process since a high calcium concentration causes formation of vanadium bearing calcium compounds that are insoluble to the subsequent leaching process. Vanadium that is not leached cannot be recovered in the leaching process. Accordingly in the presence of calcium the vanadium losses in the subsequent leaching stage are too high to reach economical process.

#### 30 **Example 9**

In accordance with the present process, when calcium depleted material is fed to the roasting the calcium content is significantly lower and the losses of vanadium are significantly lower. It has been studied that with slag calcium-vanadium ratio is no higher than 0.42 calculated as CaO and V<sub>2</sub>O<sub>5</sub> respectively the

vanadium recovery of 93% can be achieved in the subsequent leaching process. This ratio would be achieved with calcium rich feed material used in the previous examples when 97% w/w of calcium is removed in the calcium removal stage.

### Conclusions

- 5                    The results of the Examples 1 to 7 are shown in Table 1. As can be seen, the use of calcium removed slag provides lower smelting power requirement and lower Si level in hot metal. Also slag vs. metal ratio is lower when using calcium removed slag.

**Table 1**

| # | Smelting power requirement<br>MW | Slag/metal<br>ratio | V in hot metal<br>% | Si in hot metal<br>% |
|---|----------------------------------|---------------------|---------------------|----------------------|
| 1 | 48                               | 4.4                 | 8.1                 | 10.9                 |
| 2 | 52                               | 4.6                 | 7.5                 | 9.6                  |
| 3 | 67                               | 5.8                 | 7.1                 | 9.0                  |
| 4 | 24                               | 1.6                 | 8.8                 | 3.3                  |
| 5 | 30                               | 2.3                 | 8.4                 | 4.7                  |
| 6 | 35                               | 2.3                 | 8.8                 | 3.4                  |
| 7 | 71                               | 0.6                 | 2.4                 | 1.0                  |

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It will be obvious to a person skilled in the art that, as the technology advances, the inventive concept can be implemented in various ways. The invention and its embodiments are not limited to the examples described above but may vary within the scope of the claims.

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## CLAIMS

1. A process for recovering metal(s) from calcium rich iron containing material, comprising

(a) leaching calcium one or more times from said calcium rich iron containing material to obtain a calcium depleted iron containing material; and

(b) subjecting the calcium depleted iron containing material to pyrometallurgical treatment to recover metal(s) from said calcium depleted iron containing material.

2. A process as claimed in claim 1, wherein the calcium rich iron containing material is slag, in particular LD slag.

3. A process as claimed in claim 1 or 2, wherein the calcium rich iron containing material comprises at least 20% w/w, preferably at least 25% w/w, more preferably at least 30% w/w, calcium.

4. A process as claimed in any one of claims 1 to 3, wherein the calcium containing material comprises at least 5% w/w, preferably at least 10% w/w, more preferably at least 15% w/w, iron.

5. A process as claimed in any one of claims 1 to 4, wherein the calcium rich iron containing material further comprises vanadium.

6. A process as claimed in claim 4, wherein the calcium rich iron containing material comprises at least 0.2% w/w, preferably 0.5% w/w, more preferably at least 1% w/w, even more preferably at least 1.5% w/w, vanadium.

7. A process as claimed in any one of claims 1 to 6, wherein vanadium and/or iron are recovered from the calcium rich iron containing material.

8. A process as claimed in any one of claims 1 to 7, wherein the pyrometallurgical treatment (b) is at least smelting or roasting.

9. A process as claimed in claim 8, wherein (b) the calcium depleted iron containing material is subjected to smelting to recover metal(s) from the calcium depleted iron containing material.

10. A process as claimed in claim 8 or 9, wherein (b) the calcium depleted material is subjected to roasting to recover metal(s) from the calcium depleted material.

11. A process as claimed in any one of claims 1 to 10, wherein the process further comprises (d) bubbling carbon dioxide containing gas into the calcium rich leaching solution obtained from stage (a) to precipitate calcium carbonate and thus to remove calcium from said calcium rich leaching solution to

obtain a regenerated calcium poor leaching solution; and (e) recycling the regenerated calcium poor leaching solvent to stage (a).

12. A process as claimed in claim 10, wherein before stage (d) the calcium rich leaching solution is (c) first filtered to remove residual calcium rich iron containing material from said calcium rich leaching solution.

13. A process as claimed in any one of claims 1 to 12, wherein the leaching solutions for leaching calcium from the calcium containing material in stage (a) is selected from the group consisting of acetic acid, nitric acid, propionic acid, aqueous solutions of ammonium salts, such as aqueous solution of ammonium acetate ( $\text{CH}_3\text{COONH}_4$ ), ammonium chloride ( $\text{NH}_4\text{Cl}$ ) or ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ).

14. A process as claimed in any one of claims 1 to 13, wherein the amount of calcium in the calcium depleted iron containing material is below 25% w/w, preferably below 20% w/w, more preferably below 15% w/w, even more preferably below 10% w/w, most preferably below 1% w/w.

15. A process for recovering vanadium from LD slag, comprising  
(o) providing LD slag;

(i) leaching calcium one or more times from said LD slag to obtain calcium depleted LD slag; and

(ii) subjecting the calcium depleted LD slag to pyrometallurgical treatment to recover iron and vanadium from the calcium depleted LD slag.

Figure 1

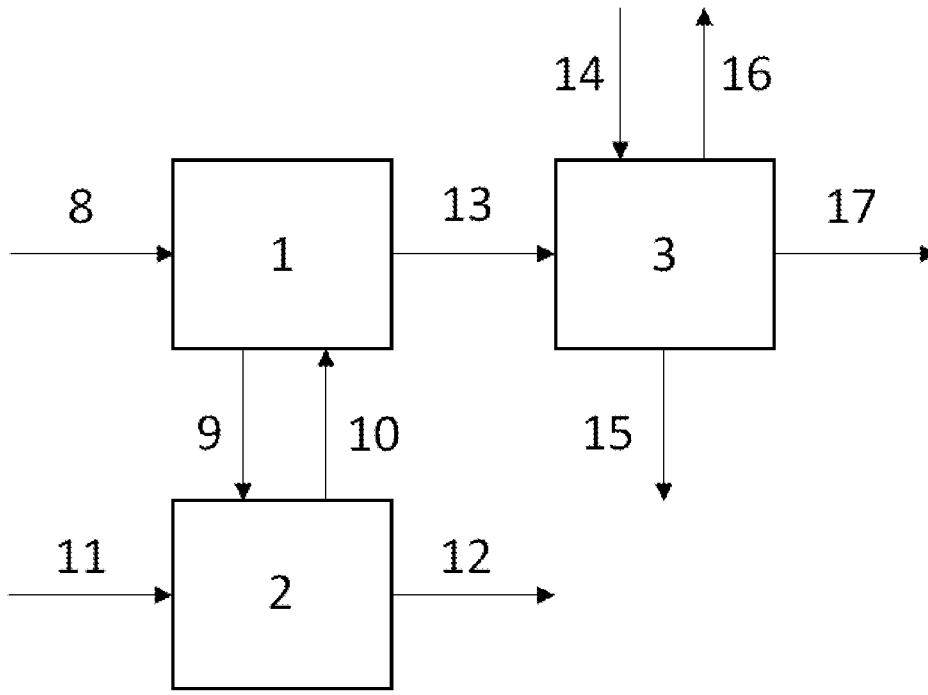


Figure 2

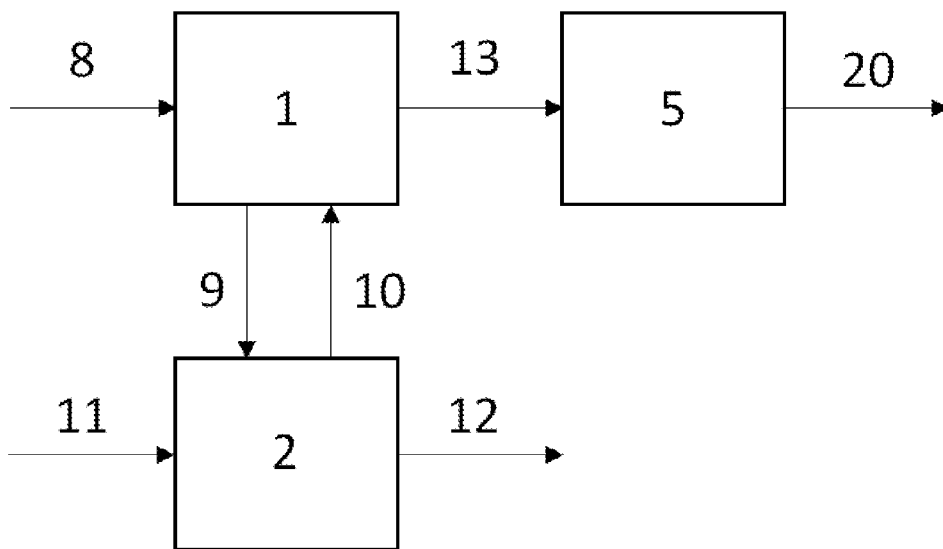


Figure 3

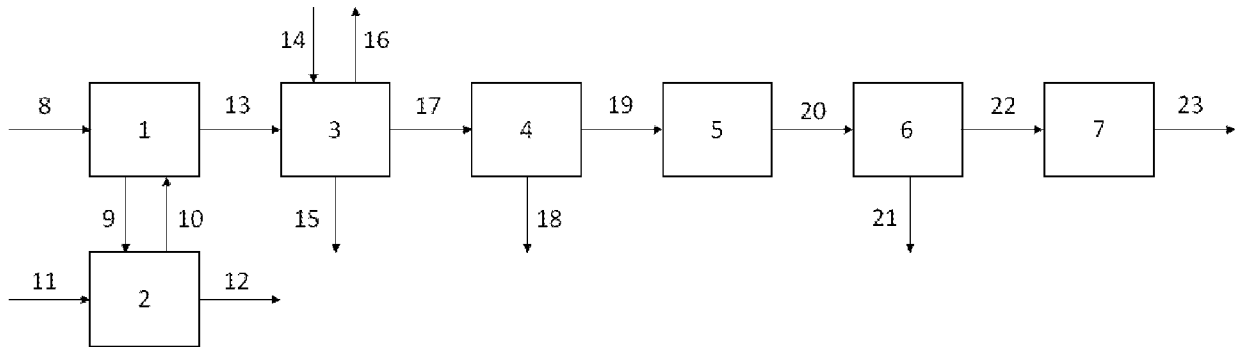
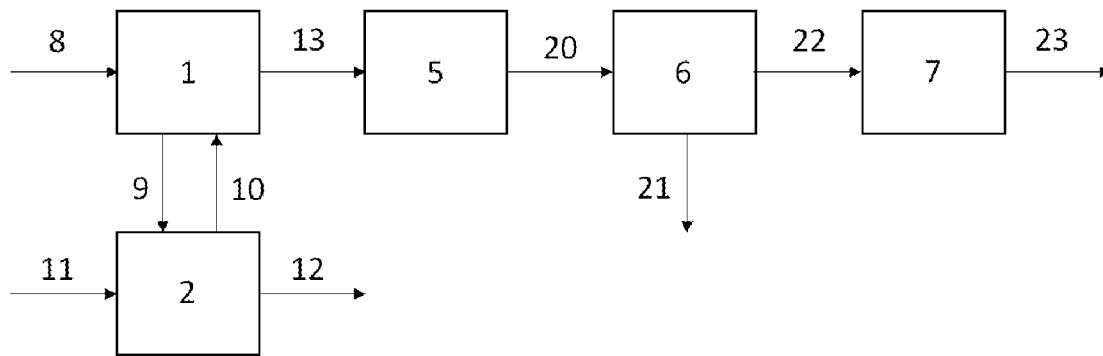


Figure 4



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI2016/050179

| <b>A. CLASSIFICATION OF SUBJECT MATTER</b>  |  |                           |
|---|--|---------------------------|
| See extra sheet   |  |                           |
| According to International Patent Classification (IPC) or to both national classification and IPC   |  |                           |
| <b>B. FIELDS SEARCHED</b>   |  |                           |
| Minimum documentation searched (classification system followed by classification symbols)   |  |                           |
| IPC: C22B   |  |                           |
| Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched   |  |                           |
| FI, SE, NO, DK  |  |                           |
| Electronic data base consulted during the international search (name of data base, and, where practicable, search terms used)   |  |                           |
| EPO-Internal, WPIAP, XPAIP, XPESP, XPIOP, XPIPCOM, XPMISC, XPOAC, XPRD, XPTK, COMPDX, INSPEC, PUBCOMP, PUBSUBS, TDB, NPL, Google  |  |                           |
| <b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>   |  |                           |
| Category*   | Citation of document, with indication, where appropriate, of the relevant passages   | Relevant to claim No.     |
| X   | WO 9608585 A1 (METALS RECYCLING TECH [US])<br>21 March 1996 (21.03.1996)<br>abstract; page 6, lines 4-11; page 11, table 1; page 28, lines 15-23   | 1, 4, 7-10, 13,<br>14     |
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| * Special categories of cited documents:  | "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  |                           |
| "A" document defining the general state of the art which is not considered to be of particular relevance  | "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   |                           |
| "E" earlier application or patent but published on or after the international filing date   | "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 |                           |
| "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) | "&" document member of the same patent family  |                           |
| "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  |  |                           |
| Date of the actual completion of the international search   | Date of mailing of the international search report   |                           |
| 11 July 2016 (11.07.2016)   | 14 July 2016 (14.07.2016)  |                           |
| Name and mailing address of the ISA/FI<br>Finnish Patent and Registration Office<br>P.O. Box 1160, FI-00101 HELSINKI, Finland<br>Facsimile No. +358 9 6939 5328         | Authorized officer<br>Ilkka Vaitiniemi<br><br>Telephone No. +358 9 6939 500  |                           |

INTERNATIONAL SEARCH REPORT

International application No.  
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CLASSIFICATION OF SUBJECT MATTER

IPC  
**C22B 3/04** (2006.01)  
**C22B 7/04** (2006.01)  
C22B 7/00 (2006.01)  
C22B 34/22 (2006.01)

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