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(54) **Title**: MAGNETIC RECOVERY OF VALUABLES FROM SLAG MATERIAL

(57) **Abstract**: The present invention relates to a process for the separation of at least one metal from a slag, comprising that at least one metal and further components, comprising at least step (A) grinding the slag, (B) if appropriate, contacting the ground slag of step (A) with at least one surface-active substance and/or at least one magnetic particle, if appropriate in the presence of at least one dispersant, resulting in formation of agglomerates of the at least one metal and the at least one magnetic particle, (C) if appropriate, addition of at least one dispersant to the mixture obtained in step (B) to give a dispersion having a suitable concentration, and (D) separation of the agglomerates from the mixture of step (B) or (C) by application of a magnetic field, and to the use of at least one magnetic particle for the separation of slag.

Magnetic recovery of valuables from slag material

Description

The present invention relates to a process for the separation of at least one metal from a slag, comprising that at least one metal and further components, comprising at least step (A) grinding the slag to obtain particles, (B) if appropriate, contacting the ground slag of step (A) with at least one magnetic particle and/or at least one surface altering substance, if appropriate in the presence of at least one dispersant, resulting in formation of agglomerates of the at least one metal and the at least one magnetic particle due to magnetic and/or hydrophobic interactions, (C) if appropriate, addition of at least one dispersant to the mixture obtained in step (B) to give a dispersion having a suitable concentration, and (D) separation of the particles from the mixture of step (A) or of the agglomerates from the mixture of step (B) or (C) by application of a magnetic field, and to the use of at least one magnetic particle for the separation of slag.

In particular, the present invention relates to a process for the separation of precious or base metals from slags resulting either from processing naturally occurring ores or from recycling existing PGM (Platinum Group Metals) containing materials, for example obtained from processes, preferably chemical processes, or automotive catalysts or from other industrial processes where a slag is produced which contains some valuables like PGMs, Cu, Mo, Co, Zn, Mn, Ni or others.

For example, the industrial precious metals Pt, Pd and Rh play a more and more important role in society. They application ranges from chemical reactions catalysis to airspace and due to their chemical and physical properties, these metals are present today in almost every aspect of our life like computers or drugs to help maintaining our environment and improve our life. One of the industrial applications of the precious metals is use for homogenous or heterogeneous catalysts, especially environmental catalysts like three way converter or diesel oxidation catalysts or for high performance materials, e. g. turbine blades or in the recent times also for jewellery and coinage.

Due to the high demand of different precious and base metals, e. g. used industrial precious metals Pt, Pd, Rh bound in automotive converter are recycled. After a rough pre-sorting and a pre-disintegration, the spent catalysts are smelted in an electric arc furnace. At approx. 1800 °C, the metals can be separated from the other materials, e. g. silica, alumina, ceria etc.

The recycling by smelting does not always take place in an electric arc furnace or induction furnace. In case of the recycling of materials bearing the so called base metals like Cu, Mo, Zn, Co, Ni etc., also flash furnaces are used working at respectably lower temperatures, for example slightly above the melting points of the metals which need to be recovered. In general, the smelting procedures, e. g. temperatures, additives, e. g. collector material like magnetite, etc. are known to the skilled artisan.

The residual material, which is obtained after removal of the valuables, is in general called furnace slag. This slag material contains typically high amounts of silicates, and other Al-, Ce-, Zr-, Fe- etc. oxides and also low amounts also of sulphides. After cooling, a very hard material is received which sometimes also contains significant amounts of valuables.

There is a strong tendency to recover the residual metals out of this slag - by re-smelting the material or by flotation processes.

The re-smelting of the slag material requires extremely high energies, because the whole slag material needs to be fed into the furnace again, whereas the concentration of the valuables is in the range of 1 to 100 ppm, or in special cases even higher. In addition, the smelting conditions need to be adjusted to the specific composition of the slag material. Therefore, pre-concentrations of the valuables from the slag are preferred.

Processes according to the prior art are based on the concentration of the valuables using flotation. Here, the valuables are selectively hydrophobized in the presence of unwanted materials. Due to their hydrophobic shell, these valuables tend to stick to air bubbles in a water-based system, and can therewith be transported to the top and then recovered. In case of slag, in particular furnace slag, this technology cannot be efficiently applied. Due to the smelting process, the metals are finely distributed and highly crystallized. Therefore, the valuables occur as extreme dense particles with unfavourable flotation characteristics, especially in combination with the comminution degree necessary for the liberation of said particles. Thus a flotation is rarely an economically successful way to recover the residual valuables from slag.

Another approach to recover the residual metals is the leaching process. Here, the whole matrix or at least the valuables in it is dissolved in highly concentrated acids or bases. This solution is then treated chemically or electrochemically to recover the valuables. This approach consumes a high amount of chemicals and is therefore, as with flotation, very rarely an economically viable procedure for the recycling of precious or base metals.

An alternative approach for the recovery of the residual metals is the magnetic separation. A magnetic assisted separation can use magnetic particles as carrier which can much more effectively transport the dense and very fine material compared to air bubbles.

Regarding magnetic separation technologies, some prior art is given:

WO 02/0066168 A1 relates to a process for separating ores from mixtures comprising these, in which suspensions or slurries of these mixtures are treated with particles which are magnetic and/or capable of floating in aqueous solutions. After addition of the magnetic particles and/or particles capable of floating, a magnetic field is applied so that the agglomerates are separated off from the mixture. However, the extent to which the magnetic particles are bound to the ore and the strength of the bond is not sufficient for the process to be carried out with a satisfactorily high yield and effectiveness. The separation of metals from a slag material is not disclosed.

US 4,657,666 discloses a process for the enrichment of ores, in which the ore present in the gangue is treated with magnetic particles, as a result of which agglomerates are formed due to the hydrophobic interactions. The magnetic particles are hydrophobicized on the surface by treatment with hydrophobic compounds, so that attachment to the ore occurs. The agglomerates are then separated off from the mixture by means of a magnetic field. The cited document also discloses that the ores are treated with a surface-activating solution of 1% sodium ethylxanthogenate before the magnetic particle is added. In this process, separation of ore and magnetic particle is effected by the destruction of the surface-activating substance which has been applied in the form of the surface-activating solution to the ore. The separation of metals from a slag material is not disclosed in said document.

WO 2010/100180 A1 relates to an agglomerate of at least one particle P which is hydrophobicized on the surface with at least one first surface altering substance and at least one magnetic particle MP which is hydrophobicized on the surface with at least one second surface altering substance, a process for producing these agglomerates and the use of the agglomerates for separating a particle P from mixtures comprising these particles P and further components. A process for separating metals from smelter slags is not disclosed in this document.

WO 2010/097361 A1 relates to a process for separating at least one first material from a mixture comprising this at least one first material, at least one second material and at least one third material, wherein the mixture to be treated is firstly brought into contact with at least one hydrocarbon in an amount of from 0.01 to 0.4% by weight, based on the sum of mixture and at least one hydrocarbon, this mixture is further brought into contact with at least one hydrophobic magnetic particle so that the magnetic particle and the at least one first material agglomerate and this agglomerate is separated from the at least one second material and the at least one third material by application of a magnetic field and, if appropriate, the at least one first material is subsequently separated, preferably quantitatively, from the magnetic particle, with the magnetic particle preferably being able to be recirculated to the process. A process for separating metals from smelter slags is not disclosed in this document, too.

WO 2010/066770 A1 discloses a process for separating at least one first material from a mixture comprising this at least one first material in an amount of from 0.001 to 1.0% by weight, based on the total mixture, and at least one second material, in which the first material is firstly brought into contact with a surface altering substance in order to hydrophobicize it, this mixture is then brought into contact with at least one magnetic particle so that the magnetic particle and the hydrophobicized first material agglomerate and this agglomerate is separated from the at least one second material by application of a magnetic field and the at least one first material is then preferably quantitatively separated from the magnetic particle, with the magnetic particle preferably being able to be recirculated to the process. A process for separating metals from smelter slags is also not disclosed in this document.

WO 2010/007157 A1 discloses a process for separating at least one first material from a mixture comprising this at least one first material and at least one second material, in which the mixture to be separated is firstly brought into contact with at least one selective hydrophobizing agent so that an adduct is formed from the at least one hydrophobizing agent and the at least one first material, this adduct is then brought into contact with at least one magnetic particle functionalized on the surface with at least one polymeric compound having an LCST (lower critical solution temperature) at a temperature at which the polymeric compound has hydrophobic character so that the adduct and the at least one functionalized magnetic particle agglomerate, this agglomerate is separated off by application of a magnetic field and the agglomerate is subsequently dissociated by setting a temperature at which the polymeric compound has hydrophilic character. A process for separating metals from smelter slags is also not disclosed in this document.

WO 2010/007075 A1 relates to a process for separating at least one first material from a mixture comprising this at least one first material and at least one second material, in which the mixture to be separated is brought into contact with at least one bifunctional compound and at least one magnetic particle so that an adduct is formed from the at least one first material, the bifunctional compound and the at least one magnetic particle, this adduct is dispersed in a suitable suspension medium, the adduct is separated off by application of a magnetic field and the adduct which has been separated off is, if appropriate, disassociated by suitable measures in order to obtain the at least one first material. A process for separating metals from smelter slags is also not disclosed in this document.

WO 2009/065802 A2 relates to a process for separating at least one first material from a mixture comprising this at least one first material and at least one second material, in which a suspension of the mixture comprising at least one first material and at least one second material and at least one magnetic particle in a suitable suspension medium is firstly produced, the pH of this suspension is set to a value at which the at least one first material and the at least one magnetic particle bear opposite surface charges so that these agglomerate, the agglomerate obtained in this way is separated off by application of a magnetic field gradient and this agglomerate which has been separated off is dissociated by setting the pH to a value at which the at least one first material and the at least one magnetic particle bear the same surface charges in order to obtain the at least one first material. A process for separating metals from smelter slags is not disclosed in this document, too.

The documents that have been cited above preferably disclose different processes for the separation of valuables from naturally occurring ores. Processes for effective separation of metals, in particular precious metals, from slags are not disclosed in the prior art.

It is therefore an object of the present invention to provide a process by means of which at least one metal, preferably at least one precious or base metal, can be efficiently separated from slags.

It is a further object to provide such a process, in which precursors of the metals to be separated, for examples magnetic agglomerates comprising the metals to be separated and magnetic particles, which are obtained from the process according to the present invention, can directly be subjected to further work up in order to obtain the desired metals in pure form. Extra addition or removal of iron-comprising compounds, respectable magnetic compounds, may be avoided or reduced.

Another object of the present invention is to provide a process for separation of at least one metal from a slag material, wherein magnetic components which are already present in the slag to be separated and which are associated with the at least one metal, are collected using a suitable magnetic separator.

These objects are solved by the present invention being a process for the separation of at least one metal from a slag, comprising that at least one metal and further components, comprising at least the following steps:

(A) grinding the slag to obtain particles,

(B) if appropriate, contacting the ground slag of step (A) with at least one magnetic particle and/or at least one surface-altering substance, if appropriate in the presence of at least one dispersant, resulting in formation of agglomerates of the at least one metal and the at least one magnetic particle due to magnetic and/or hydrophobic interactions,

(C) if appropriate, addition of at least one dispersant to the mixture obtained in step (A) or (B) to give a dispersion having a suitable concentration, and

(D) separation of the particles from the mixture of step (A) or of the agglomerates from the mixture of step (A), (B) or (C) by application of a magnetic field.

A very specific feature of the process according to the present invention is that magnetic particles are used for recovering valuables from the smelter slag by magnetic separation. In general, smelting processes for enriching precious metals or base metals are conducted using mixtures or agglomerates of these precious metals or base metals and iron comprising compounds. With the process according to the present invention it is preferably possible to obtain particles or agglomerates comprising iron comprising compounds like magnetite and metals after magnetic separation. These particles or agglomerates can directly be used in smelting processes for obtaining precious metals in a form which can be fed into the refinery. After the smelting, the concentrate with the valuables in general needs to be refined to get the pure metals. With the process according to the present invention, further steps like separating the particles or agglomerates after magnetic separation and/or addition of extra iron comprising compounds prior to smelting can be avoided: The magnetite used as carrier within the process given in the present invention can be adjusted to the composition for smelting process. With the process according to the present invention, iron comprising particles or agglomerates can be obtained which carry a suitable and advantageous amount of iron which is necessary to obtain metals in pure form by smelting. The process according to the present invention therewith combines two process steps - the magnetic concentration of residual valuables from smelter slag material and the addition of collector, which is needed for an efficient smelting process. This combination is unique and not described in any literature.

In addition, with the process according to the present invention magnetic material which is already present in the slag to be separated and which is associated with the desired at least one metal can be used in order to obtain the at least one metal by magnetic separation.

The process according to the present invention is conducted in order to separate at least one metal from any slag, e. g. smelter slag, furnace slag or other slag materials. Slag can be defined as products from secondary process from metallurgical processes or residues from combustion processes.

The single steps of the process according to the present invention and general and preferred embodiments of the single components used and present in the process according to the present invention are explained in detail in the following:

The process according to the present invention is conducted in order to separate slag, for example smelter slag or furnace slag. These materials are in general known to the skilled artisan.

In a preferred embodiment, the slag which is treated according to the present invention, is selected from furnace slag, for example resulting from processing concentrates from platinum group metals (PGMs) bearing ores, spent catalyst materials or mixtures thereof.

In a preferred embodiment of the process according to the present invention, the slag that is introduced into step (A) is an artificially prepared slag. Slag that is introduced into step (A) of the process according to the present invention is preferably not naturally occurring like ores, but is artificially prepared.

Therefore, the present invention preferably relates to the process according to the present invention, wherein the slag that is introduced into claim (A) is an artificially prepared slag.

The main use of a smelting process is to convert an ore or scrap or material mixture containing different metals into a form, from which the desired metals can be skimmed as a metal layer and the undesired metal oxides, e.g. silicates, alumina, etc., remain as the slag. In general, one can distinguish between oxidative and reductive smelter operation. The slag material that is to be separated according to the present invention can either be obtained under reductive conditions or can be obtained under oxidative conditions.

For example, slag produced in PGM recovery operations, for example Pt mines, old catalyst reprocessing etc., is usually formed under reducing conditions, which are exemplarily explained in the following. The energy needed to heat the mass to beyond the melting point is in general provided by an external heating, e.g. gas burners, or an electric arc. Often, carbon or other reducing materials are added. The goal is to reduce noble metal compounds to metal state. Reduced metals and the oxidic phase are immiscible and demix. Slags produced under reductive conditions often contain residual PGMs as free metals or alloys with other transition metals, particularly iron. These alloys are often ferromagnetic and can be separated from the slag matrix by a magnetic field after liberation. The losses of PGM into slag are almost exclusively due to incomplete demixing of the liquid metal and liquid slag phases - no significant formation of PGM solid solution in the slag occurs.

In a smelter that is operated under reductive conditions the most base metals sulphides remain as sulphides. Some metal species, e.g. the precious group metals, may also remain as the native metal or tend to migrate into the magnetic fraction. Magnetite is often fed into the smelter to support the formation of the slag. Platinum and also Rhodium preferably feature this behaviour to migrate to the magnetic fraction thus after the smelting process these precious group metals are hidden in the magnetic fraction, which is preferably in the slag, as dopants. In this scenario, the magnetic separation process according to the present invention can be used directly without any additional steps. The final operation depends of the composition of the slag, for example:

(1) If Pt, Rh are the metals of most interest and magnetite is feed into the smelter, than very often a pure magnetite separation without the addition of additional magnetite after the grinding step (A) is sufficient to recover the metals of value.
(2) If Ni, Cu and other base metals are the metals of the most interest a surface altering compound for metal sulphides is preferably added, in particular xanthates, dithiophosphates or carbamates according to general formula (I), to hydrophobize these species. In a next step, hydrophobized magnetite is added and forms hydrophobic agglomerates. Due to its magnetism these hydrophobic agglomerates containing magnetite and the metal sulphides can be separated magnetically. In this case, a collector and also hydrophobic magnetite is preferably added after the grinding step (A), but before the magnetic separation step (D).
(3) If the metals of interest are the precious group metals and the base metals, these two scenarios according to (1) and (2) can be combined which results in an operation described under (2).

Is a smelter operated under oxidative conditions, the base metals sulphides and also some native metals compounds are oxidized. In this case, the magnetic separation process according to the present invention can only be used exceptionally without pretreatment. However, if a surface treatment, for example a selective sulphidization of the desired metal of value, is executed, the magnetic separation process according to the present invention can be employed as described herein. Besides the preferred sulphidization, also other surface treatments can be used to convert the desired metal species into a sulphidic, native or magnetic form. These treatments are known to the skilled artisan.

A further point that may influence the process for separation of at least one metal from a slag according to the present invention, in particular the process steps that have to be conducted in a preferred embodiment, is the method how the slag material is treated, in particular cooled, after smelting.

In general, after reductive or oxidative smelting, the metal phase is skimmed and the slag is further treated, e.g. by granulation. Before the following steps, in particular the steps of the process according to the present invention, the slag must cool down.

If, in a first embodiment, the slag is exposed to room temperature for cooling for a longer period of time, for example several days, preferably different discrete domains of different compositions are formed. These different domains can be detected by methods that are known to the skilled artisan, for example using X-ray based methods like SEM. According to this method, the heavier elements can be detected as light dots embedded in an oxidic matrix containing mainly of Mg, Al, Si, O, for example

The size of the domains can, for example, be influenced by the cooling time. Is the slag allowed to cool down to room temperature without any other influence like addition of water etc., according to a first embodiment of the present invention, the above mentioned domains can grow and form domains in the micro meter range. According to this embodiment, the particularly preferred process according to preferred alternative 1 or 2 as explained in the following can be conducted. In general, the slower the slag cools, the bigger are the domains and with that also e.g. the magnetite containing domains. As described above, the magnetite containing domains feature also some precious group metals. The bigger theses magnetic domains, the easier can these species be separated by a magnetic separation according to alternatives 1 or 2 as explained in the following. A lower limit for the size of the magnetic domains for this embodiment is for example 1 µm,

In a second embodiment, the slag is cooled very rapidly (shock cooled) after smelting, for example by contacting with water, for example by transporting the slag into a concrete vessel with water. According to this embodiment, the domains are not allowed to grow and the slag that is obtained is very close to a solid solution and the different metals and elements are only very rarely allowed to form isolated domains.

If a slag is produced according to this second embodiment, the process for separation according to the present invention can also be used, in particular according to preferred alternative 2 or 3 as explained in the following.

The slag, preferably furnace slag, which is preferably employed in the process according to the present invention is preferably obtained from melting processes known to the skilled artisan, for example to obtain metals like Mo, Cu, Ni, Ag, Hg, Au, Pt, Pd, Rh, Ru, Ir, Os or mixtures thereof. For example, electric arc smelting is used in these furnaces and is further employed in process such as smelting of scrap iron.

In a preferred embodiment the at least one metal which is to be separated from the slag according to the present invention is selected from the group consisting of Ag, Au, Pt, Pd, Rh, Ru, Ir, Os, Cu, Mo, Ni, Mn, Zn, Pb, Te, Sn, Hg, Re, V, Fe and mixtures thereof. In principle, these metals may be present in elemental form or as compounds, for example in oxidic and/or sulfidic form, as a binary compound or a component in a multimetal compound. In a further embodiment of the present invention the mentioned precious metals are present in form of metal compounds, like for example, alloys with other metals e. g. Fe, Cu, Ni, Pb, Bi, with each other, and/ or compounds with nonmetals e.g. phosphides, arsenides, sulphides, selenides, tellurides etc. Particularly preferred metal compounds are metal alloys.

The present invention therefore preferably relates to the process according to the present invention, wherein the at least one metal is selected from the group consisting of Ag, Au, Pt, Pd, Rh, Ru, Ir, Os, Cu, Mo, Ni, Mn, Zn, Pb, Te, Sn, Hg, Re, V, and mixtures thereof, for example alloys with each other or with elements like Fe, Ni, Pd etc. thereof.

Preferably the present invention relates to the process according to the present invention, wherein the at least metal is selected from PGM, wherein PGM is the abbreviation of Precious Group Metals, being Au, Pt, Ir, Pd, Os, Ag, Hg, Rh, Ru, in particular Au, Pt, Pd, Rh, further preferred Pt, Pd, Rh.

The furnace slag that is preferably used in the process according to the present invention is obtained as a product, for example an end-product, a by-product and/or and a waste-product of smelting processes. During smelting, a silicate-rich liquid phase separates from the heavier metal melt. The latter is flowing through dedicated openings in the melting vessel and is further processed. The phase separation is however not complete, but a fraction of the desired metal becomes trapped in the liquid slag phase and remains dispersed there after solidification resulting in a so called mixing layer. In a preferred embodiment of the present invention the smelter slag that is obtained from this mixing layer is preferably treated by the process according to the present invention.

In a preferred embodiment of the present invention, the slag, preferably the furnace slag, that is used is a solid solution and preferably comprises further components selected from the group consisting of SiO_2, CaO, Al_2O_3, MgO, P_2O_3, ZrO_2, Fe_2O_3, Fe_3O_4, CeO_2, Cr_2O_3, complex oxide matrices and mixtures thereof. These oxides are not necessarily present in the slag matrix as isolated compounds, but may only be present as complex oxides. It is common to represent a mixed metal oxide as comprised of binary oxides of the respective metals. In this text, this nomenclature shall be used. Said solid solution may be amorphous and/or glass-like, or may contain crystalline material comprised of metal oxides listed above.

A very typical composition of a furnace slag that can particularly preferably be used in the process according to the present invention comprises 5 to 80 % by weight SiO_2, 20 to 50% by weight CaO, 0 to 60 % by weight Al_2O_3, 0 to 10% by weight MgO, 0 to 10% by weight P_2O_5, 0 to 10% by weight ZrO_2, 0 to 10% by weight Fe_2O_3, and optionally other iron oxides, 0 to 10% by weight CeO_2, and optionally other components.

The present invention therefore preferably relates to the process as mentioned above, wherein the slag comprises at least one compound selected from the group consisting of SiO_2, CaO, Al_2O_3, MgO, P_2O_3, ZrO_2, Fe_2O_3, Fe_3O_4, CeO_2, Cr_2O_3, complex oxide matrices and mixtures thereof.

The further components that are present in the slag that is separated according to the present invention are obtained after a smelting process of corresponding precursors. A difference between the slag that is separated according to the present invention and naturally occurring ores is that the slag according to the present invention is not obtained from natural sources but is obtained from artificial processes.

In addition to the compounds as mentioned above the slag to be treated according to the present invention, may contain further components like for example lead- and/or iron-containing compounds and/or lead and/or iron in metallic form. In a preferred embodiment iron containing compounds like magnetite are present in the slag to be separated. In this preferred embodiment, step (B) of the process according to the present invention may be skipped, and the desired at least one metal is separated magnetically as an agglomerate with magnetic components which have already been present in the slag.

The slag to be treated with the process according to the present invention comprises the at least one metal, particularly the preferred metals as mentioned above, preferably in an amount of 0.01 to 1000 g / t, preferably 0.01 to 500 g / t, slag. Slag materials containing the desired at least one metal in lower or higher amounts are also within the scope of the present invention.

In a first preferred embodiment of the present invention, the at least one metal to be separated from the slag, is present in an amount of 0.01 to 1000 g/t slag, for the at least one metal being selected from the group of precious metals like Ag, Au, Pt, Pd, Rh, Ru, Ir, Os, Zn, Pb, Te, Sn, Hg, Re, V or Fe and / or the base metals sulphides of Cu, Mo, Ni and Mn or others. Slag materials comprising the desired at least one metal in lower or higher amounts are also within the scope of the present invention.

The individual steps of the process of the invention are described in detail below:

Step (A):

Essential step (A) of the process according to the present invention comprises grinding the slag to obtain particles.

In step (A) of the process according to the present invention, the slag which is preferably obtained from generally known smelting processes is ground in order to obtain slag particles having a suitable particle size for the further process steps.

In a preferred embodiment of the process of the invention, the slag to be treated according to the present invention is ground to obtain particles having a d_{80} of 100 µm or less, for example a d_{80} of 100 nm to 100 µm. The wording “d_{80}” is generally known to a person having ordinary skill in the art, meaning that 80% of particles being present in the mixture have a diameter of less than the mentioned value.

The present invention therefore relates to the process according to the present invention, wherein in step (A) the slag is ground to a d_{80} of 100 µm or less.

In a preferred embodiment, step (A) is conducted by milling, in particular by ball milling. Suitable processes and apparatuses are in general known to those skilled in the art, for example wet milling in a stirred or rolling ball mill.

In a further preferred embodiment, the particles are sieved into fractions having the desired particle size, after milling, with the oversize fraction optionally being returned into the milling process.

Grinding according to step (A) of the process according to the present invention can be conducted in the presence or absence of at least one dispersion medium. Suitable dispersion media for dispersion are for example selected from the group consisting of water, water-soluble organic compounds and mixtures thereof, particularly preferably water. If step (A) is conducted in dispersion, preference is given to using the same dispersion medium that is used in the whole process, preferably water.

In one embodiment of the process according to the present invention, step (B) is conducted after step (A). In this case, in general, it is possible that steps (A) and (B) are at least partially conducted at the same time, for example the slag that is to be separated according to the present invention can be contacted with at least one surface altering substance and/or at least one magnetic particle during milling. Details of this preferred embodiment are mentioned below.

In another preferred embodiment of the process according to the present invention, step (B) is not conducted after step (A). This embodiment is preferred, if the slag that is to be treated according to the present invention comprises magnetic substances itself, so that after grinding magnetic particles are obtained comprising the desired metal and magnetic substances. According to this embodiment, the addition of further magnetic particles and/or surface altering substances is not necessary.

In a particularly preferred embodiment of the process according to the present invention, after step (A) at least one dispersant is added to the mixture obtained in step (A) to give a dispersion having a suitable concentration. According to the present invention, this optional step is called step (A1).

Therefore, in particular, the present invention relates to the process according to the present invention, wherein after step (A) step (A1) is conducted, comprising

(A1) Addition of at least one dispersant to the mixture obtained in step (A) to give a dispersion having a suitable concentration.

Step (A1) is preferably conducted, if step (A) of the process according to the present invention is conducted in bulk.

Step (A1) is preferably conducted, if non-hydrophobized magnetite is added in step (B). According to this embodiment, step (C) of the process according to the present invention is preferably not conducted.

Suitable dispersion media are all dispersion media which have been mentioned above in respect of step (A). A particularly preferred dispersion medium which is added in step (A1) of the process according to the present invention is water, optionally mixed with at least one polar organic solvent that have been mentioned in respect of step (A).

Thus, step (A1) comprises either converting the mixture present in bulk from step (A) into dispersion or converting the mixture which is already in dispersion from step (A) into a dispersion of lower concentration by addition of dispersion media.

According to the invention, the amount of dispersion medium added in step (A1) can generally be selected so that a dispersion which is readily stirrable and/or conveyable is obtained.

In a preferred embodiment, the amount of dispersion medium that is added in step (A1) of the process according to the present invention is determined to obtain a dispersion having a solid content of 1 to 80 % by weight, preferably 10 to 45 % by weight, particularly preferably 30 to 40 % by weight, in each case based on the whole amount of solids that have to dispersed.

The addition of dispersion medium in step (A1) of the process of the invention can, according to the invention, be carried out by all methods known to those skilled in the art.

Step (B):

Step (B) of the process according to the present invention is an optional step.

In a preferred embodiment step (B) is not conducted, but is skipped. In this embodiment, the slag to be separated is ground in step (A) to obtain particles, if appropriate, at least one dispersant is added in optional step (C), and the particles are magnetically separated in step (D). Step (B) can be skipped if magnetic particles are present in the slag to be separated, which are interconnected with the desired at least one metal. In this case, no further magnetic particles and/or surface altering substances have to be added (alternative 1). This embodiment of the process according to the present invention is preferably conducted, if a slag is separated according to the present invention that is obtained by slow cooling and that therefore comprises domains of magnetic material. This preferred process according to the present invention comprises steps (A), (C) and (D).

In another preferred embodiment, it is further possible that step (B) is conducted although magnetic particles are present in the slag to be separated, if the susceptibility of the magnetic particles present in the slag is not high enough to be separated efficiently by magnetic field gradient. Then, magnetite particles are added. Due to magnetic - magnetic interactions, stronger magnetism is achieved at the original very weak magnetic particles which can then be separated magnetically. In this embodiment, preferably no surface altering substance needs to be added (alternative 2). This embodiment of the process according to the present invention is preferably conducted, if a slag is separated according to the present invention that is obtained by rapidly (shock) cooled slags generated under reductive conditions. This further preferred process according to the present invention comprises steps (A), (A1), (B) and (D).

In another preferred embodiment of the process according to the present invention, step (B) is conducted, if the slag to be separated comprises no magnetic particles or not enough magnetic particles in the surrounding of the valuables. In this case at least one surface altering substance is added in step (B) of the process according to the present invention in order to hydrophobize the at least one first metal in the presence of the undesired further components. Furthermore, hydrophobized magnetic particles are added. In a further embodiment, unhydrophobized magnetic particles are added in combination with at least one compound for hydrophobizing the magnetic particle, in order to attach to the magnetic particle surface to make it hydrophobic in situ. Due to hydrophobic interaction between the hydrophobized at least one metal and the hydrophobized magnetic particle, the hydrophobized magnetic particle stick to the hydrophobized at least one metal. These hydrophobic agglomerates can be separated magnetically (alternative 3). This embodiment of the process according to the present invention is preferably conducted, if a slag is separated according to the present invention that is obtained by rapid cooling, for example by addition of water to the hot slag. This further preferred process according to the present invention comprises steps (A), (B), (C) and (D).

In the following, the embodiment that step (B) is conducted, is explained in detail:

Step (B) of the process according to the present invention comprises contacting the ground slag of step (A) with at least one magnetic particle and/or at least one surface-altering substance, if appropriate in the presence of at least one dispersant, resulting in formation of agglomerates of the at least one metal and the at least one magnetic particle due to magnetic and/or hydrophobic interactions. The magnetic particle which is present in the particles or agglomerates may be added in step (B) and/or may already be present in the slag to be separated.

In a first preferred embodiment of step (B) of the process according to the present invention, the ground slag that is obtained from step (A) of the process according to the present invention is contacted with at least one surface altering substance, to have that at least one surface altering substance attached to the surface of the at least one metal.

Contacting of the slag to be separated according to this first embodiment can be accomplished in any suitable reactor known to the skilled artisan. In a preferred embodiment, this contacting is accomplished in a mill, preferably in a centrifugal, rolling or stirred ball mill, or in a T-tube, T-jet or Y-jet. In a preferred embodiment grinding to obtain suitable particle sizes according to step (A) and the addition of at least one surface altering substance is done at the same time and/or in the same apparatus, for example in the same mill, preferably consecutively, and optionally interrupted by classification, e.g. by a sieve or a hydrocyclone.

In an alternative embodiment, the contacting can take place in an apparatus deigned to exert a strong shear force on particles in a suspension, such as a T- or Y-jet, or T-tube.

In a second embodiment of step (B) of the process according to the present invention, the ground slag that is obtained from step (A) of the process according to the present invention is brought into contact with at least one surface altering substance, to have that at least one surface altering substance attached to the surface of the at least one metal, and is further brought into contact with at least one magnetic particle that can optionally be hydrophobized at the surface.

Contacting of the slag to be separated according to this second embodiment can also be accomplished in any suitable reactor known to the skilled artisan. In a preferred embodiment, this contacting is accomplished in a mill, preferably in a centrifugal, rolling or stirred ball mill. In a preferred embodiment grinding to obtain suitable particle sizes according to step (A) and the addition of at least one surface altering substance and of at least one magnetic particle is done at the same time and/or consecutively in the same apparatus, for example in the same mill, preferably consecutively, and optionally interrupted by classification, e.g. by a sieve or a hydrocyclone.

In a further preferred embodiment the at least one magnetic particle that is added in step (B) of the process according to the present invention is hydrophobized. In a preferred embodiment of the process according to the present invention the compound which is needed for hydrophobizing the at least one magnetic particle is added during grinding, before or after addition of the at least one magnetite and/or before or after addition of the at least one surface altering substance.

In a further embodiment of the process according to the present invention, a compound for hydrophobizing the at least one magnetic particle is added in step (B), if the at least one magnetic particle is not added in step (B), but is already present in the slag to be separated. In this embodiment the at least one magnetic particle that is already present in the slag to be separated is hydrophobized.

In a particularly preferred embodiment of the process according to the present invention the slag to be treated according to the present invention is contacted with at least one surface altering substance and the at least one hydrophobized magnetic particle at the same time. In another preferred embodiment, the magnetic particle is hydrophobized before contacting with the slag to be treated and with the at least one surface altering substance.

If the at least one metal is hydrophobized using at least one surface altering substance, preferably at least one magnetic particle is used which is also hydrophobized at its surface.

According to the present invention the wordings “surface active” and “surface altering” are used in an equivalent way. For the purposes of the present invention, a “surface altering substance” or ”surface active substance” is a substance which is able to alter the surface of the particle to be enriched in the presence of the other particles which are not to be enriched in such a way that afterwards an attachment of a hydrophobic particle by means of hydrophobic interactions can occur, preferably by rendering the surface of the first particle hydrophobic. Surface altering substances which can be used according to the invention become attached to the at least one metal and produce a suitable hydrophobicity of the at least one metal.

Preferred surface altering compounds for use in step (B) of the process according to the present invention are selected from the group of surface altering substances of the general formula (I)

$$A\text{-}Z \quad (I)$$

which becomes attached to the at least one first material, where

A is selected from among linear or branched C_1-C_{30}-alkyl, C_1-C_{30}-heteroalkyl, optionally substituted C_6-C_{30}-aryl, optionally substituted C_6-C_{30}-heteroalkyl, C_6-C_{30}-aralkyl, and

Z is a group by means of which the compound of the general formula (I) binds to the at least one hydrophobic material.

In a particularly preferred embodiment, A is a linear or branched C_4-C_{12}-alkyl, very particularly preferably a linear C_4- or C_8-alkyl. Heteroatoms which may be present according to the invention are selected from among N, O, P, S and halogens such as F, Cl, Br and I.

In a further particularly preferred embodiment, X is selected from the group consisting of anionic groups $-(X)_n-PO_3^{2-}$, $-(X)_n-PO_2S^{2-}$, $-(X)_n-POS_2^{2-}$, $-(X)_n-PS_3^{2-}$, $-(X)_n-PS_2^{-}$, $-(X)_n-POS^{-}$, $-(X)_n-PO_2^{-}$, $-(X)_n-PO_3^{2-}$ $-(X)_n-CO_2^{-}$, $-(X)_n-CS_2^{-}$, $-(X)_n-COS^{-}$, $-(X)_n-C(S)NHOH$, $-(X)_n-S^{-}$ where X is selected from the group consisting of O, S, NH, CH_2 and n = 0, 1 or 2, with, if appropriate, cations selected from the group consisting of hydrogen, NR_4^+ where the radicals R are each, independently of one another, hydrogen or C_1-C_8-alkyl, an alkali metal or an alkaline earth metal. The anions mentioned and the corresponding cations form, according to the invention, uncharged compounds of the general formula (I).

Particularly preferred surface altering substances which are used in step (A) of the process of the present invention are C_1-C_{20}-xanthates, for example octyl xanthate, C_2-C_{20}-dithio- or thionocarbamates and C_1-C_{20}-dithiophosphates.

Moieties A and/or functional group Z which selectively attach to the at least one metal being present in the slag to be separated can in general be selected from the embodiments as mentioned above. In particular, the nature of compounds according to general formula (I) comprising functional group Z is preferably selected in respect of the nature of the slag, i. d. nature and amount of compounds present in said slag.

In a preferred embodiment, a mixture comprising more than one surface altering compound selected from compounds according to general formula (I) is used in order to treat the slag according to the present invention. The composition of this mixture can be determined by a person having ordinary skill in the art.

The at least one magnetic particle that is used according to the present invention is preferably an iron-comprising compound, for example an iron-oxide. Suitable iron-comprising magnetic compounds are in general known to the skilled artisan.

In a particular preferred embodiment of the process according to the present invention the at least one magnetic particle is magnetite Fe_3O_4. In a further embodiment of the present invention the at least one magnetic particle may be doped with at least one dopant. Suitable and preferred dopants are selected from the group consisting of Co, Ni, Zn and mixtures thereof. The at least one dopant is preferably present in an amount of 0.1 to 5 % by weight, in respect of the at least one magnetic particle. One reason for the presence of at least one dopant is an increase of the magnetic properties of the magnetic material.

Magnetite is known to the skilled artisan and is commercially available. Furthermore, processes for the preparation of magnetite are known to those skilled in the art. Furthermore, the positive impact of magnetite in the smelting process has been discussed above. However, the combination of using magnetite as a collector for the residual valuables and a smelting additive has been also discussed above.

The at least one magnetic particle that is used in accordance with the present invention has in general an average diameter that enables this particle to efficiently agglomerate with the at least one first material. In a preferred embodiment the magnetic particle has a d_{80} 1 nm to 10 mm. The particle size of the magnetite can be reduced within the process by the grinding or milling.

An advantage of the use of at least one iron-comprising magnetic particle, preferably magnetite, is that after magnetic separation according to step (D) of the process according to the present invention, an agglomerate comprising the desired at least one metal and an iron-comprising compound are obtained which can preferably directly be transferred into a further smelting process. In smelting processes for obtaining precious metals, in general iron has to be added in order to obtain the precious metals in high purity. With the present invention, the right amount of iron to obtain high purity and yield can easily be adjusted.

In a preferred embodiment, the at least one magnetic particle is hydrophobized at the surface by at least one hydrophobic compound. As mentioned above the at least one hydrophobic compound can be added at any stage of step (A) and/or (B) of the process according to the present invention. In a further embodiment, already hydrophobized magnetic particles can be introduced.

In a preferred embodiment the at least one magnetic particle, which is already present in the slag to be separated and/or can be added in step (B) of the process according to the present invention, is hydrophobized in a way that the surface characteristics of said particle are altered in a way that the contact angle of the hydrophobized magnetic particle is preferably more than 30°, preferably more than 60°, particularly preferably more than 160°.

The hydrophobic compound for hydrophobizing the at least one magnetic particle is preferably selected from among compounds of the general formula (II)

B-Y (II),

where

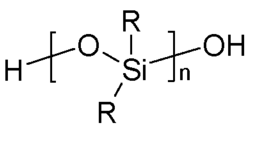
B is selected from among linear or branched C_2- or C_3-C_{30}-alkyl, C_2- or C_3-C_{30}-heteroalkyl, optionally substituted C_6-C_{30}-aryl, optionally substituted C_6-C_{30}-heteroalkyl, C_6-C_{30}-aralkyl, and

Y is a group by means of which the compound of the general formula (II) binds to the at least one magnetic particle.

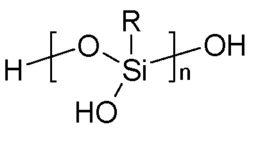
In a particularly preferred embodiment, B is a linear or branched C_6-C_{18}-alkyl, preferably linear C_8-C_{12}-alkyl, very particularly preferably a linear C_{12}-alkyl. Heteroatoms which may be present according to the invention are selected from among N, O, P, S and halogens such as F, Cl, Br and I.

In a further particularly preferred embodiment, Y is selected from the group consisting of $-(X)_n-Z_3$, $-(X)_n-HZ_2$, $-(X)_n-H_2Z$ where Z is F, Cl, Br, I, OH, and anionic groups such as $-(X)_n-SiO_3^{3-}$, $-(X)_n-CO_2^-$, $-(X)_n-PO_3^{2-}$, $-(X)_n-PO_2S^{2-}$, $-(X)_n-POS_2^{2-}$, $-(X)_n-PS_3^{2-}$, $-(X)_n-PS_2^-$, $-(X)_n-POS^-$, $-(X)_n-PO_2^-$, $-(X)_n-CO_2^-$, $-(X)_n-CS_2^-$, $-(X)_n-COS^-$, $-(X)_n-C(S)NHOH$, $-(X)_n-S^-$ where X = O, S, NH, CH_2 and n = 0, 1 or 2, and, if appropriate, cations selected from the group consisting of hydrogen, NR_4^+ where the radicals R are each, independently of one another, hydrogen or C_1-C_8-alkyl, an alkali metal, an alkaline earth metal or zinc, also $-(X)_n-Si(OZ)_3$ where n = 0, 1 or 2 and Z = charge, hydrogen or short-chain alkyl radical.

Further preferred hydrophobizing compounds are mono- oligo- or polysiloxanes with free OH groups, such as



(1)



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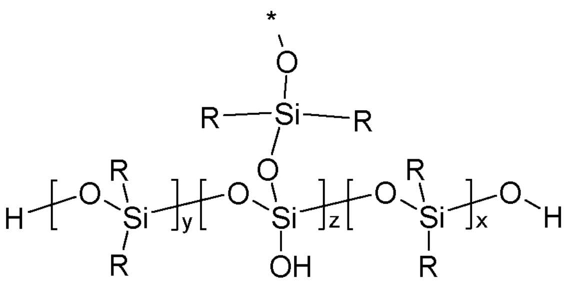

(3)

in which n, x, y, and z are independently of another 1 to 100, and R are independently of each other straight or branched alkyl groups with C_1-C_{12}.

In formula (3) * means a bonding to further moieties comprising $-SiOR_2$.

Very particularly preferred hydrophobizing substances of the general formula (II) are silicon based, silicon oils or for example siloxanes resulting from in-situ hydrolysis of dodecyl- or other alkyltrichlorosilanes or alkyltrialcoxysilanes, phosphonic acids, for example octylphosphonic acid, carboxylic acids, for example lauric acid, oleic acid or stearic acid, partly polymerized siloxanes (known as silicon oils), or mixtures thereof.

The hydrophobizing substances can in general be added to the mixture comprising the mixture that has to be separated, the at least one surface altering substance and the at least one magnetic particle. In a further embodiment the hydrophobizing substance is added to the at least one magnetic particle prior to its addition to the mentioned mixture. Preferably, in case of silicon based hydrophobizing substances, an intermediate step of in situ generating the active agent can be added, consisting of contacting the stable precursor with water for a certain period of time, for example 1 sec to 72 h, before contacting the resulting with the at least one magnetic particle.

In one possible embodiment of step (B) of the process according to the present invention, the at least one magnetic particle is added to a mixture comprising the mixture that has to be separated in dispersion. In another possible embodiment of step (B) of the process according to the present invention, the at least one magnetic particle is added to a mixture comprising the mixture that has to be separated without any dispersant. The first embodiment is preferred.

If the at least one magnetic particle is added in dispersion, in general all dispersion media in which the at least one magnetic particle is not completely soluble can be used. Suitable dispersion media for dispersion are for example selected from the group consisting of water, water-soluble organic compounds and mixtures thereof, particularly preferably water. Particular preference is given to using the same dispersion medium that is used to disperse the mixture to be separated, preferably water.

According to the invention, the amount of dispersion medium for predispersing the magnetic particles can generally be selected so that a slurry or dispersion which is readily stirrable and/or conveyable is obtained. In a preferred embodiment, the amount of mixture to be treated based on the total slurry or dispersion is between 10 and 60% by weight.

According to the invention, the dispersion of the magnetic particles can be produced by all methods known to those skilled in the art. In a preferred embodiment, the magnetic particles to be dispersed and the appropriate amount of dispersion medium or mixture of dispersion media are combined in a suitable reactor, and stirred by means of devices known to those skilled in the art, for example by means of a mechanical propeller stirrer, for example at a temperature of from 1 to 80 °C, preferably at room temperature.

In step (B) which can be combined with step (A) of the process according to the present invention, the at least one magnetic particle becomes attached to the at least one metal. The attachment between the magnetic particle and the at least one metal can be due to magnetic interactions, for example, if the at least one metal is associated with magnetic material, like for example iron oxide or any other ferromagnetic compound or it is due to hydrophobic interactions between the hydrophobized magnetite and the also hydrophobized at least one metal, or due to both.

There is generally no bonding interaction between the at least one magnetic particle and the other components which are present in the slag except the at least one metal, so that these components do not become attached to one another. Thus, addition products of the at least one metal and the at least one magnetic particle are present alongside the further other components in the mixture after step (B).

The contacting in step (B) of the process of the invention can be brought about by all methods known to those skilled in the art. Step (B) can be carried out in bulk or in dispersion, preferably in suspension, particularly preferably in aqueous suspension.

In one embodiment of the process of the invention, step (B) is carried out in bulk, i.e. in the absence of a dispersion medium.

For example, the ground slag to be treated, the at least one surface altering substance and/or the at least one magnetic particle are combined and mixed in the appropriate amounts without any dispersion medium. Suitable mixing apparatuses are known to those skilled in the art, for example mills such as ball mills. In this embodiment, step (B) can be conducted in the same apparatus as used in step (A).

In a further preferred embodiment, step (B) is carried out in a dispersion, preferably in suspension. Suitable dispersion media are all dispersion media in which the mixture from step (B) is not completely soluble. Suitable dispersion media for producing the slurry or dispersion as per step (B) of the process of the invention are selected from the group consisting of water, water-soluble organic compounds, for example alcohols having from 1 to 4 carbon atoms, and mixtures thereof, preferably water.

If step (B) of the process according to the present invention is conducted in dispersion, preferably a dispersion is used having a solid content of 1 to 60 % by weight, preferably

10 to 45 % by weight, particularly preferably 30 to 40 % by weight, in each case based on the whole amount of solids that have to be dispersed.

Step (B) of the process of the invention is generally carried out at a temperature of from 1 to 80°C, preferably from 20 to 40°C, particularly preferably at ambient temperature.

The at least one surface altering substance is generally used in an amount which is sufficient to achieve the desired effect, being the hydrophobization of the at least one metal in the presence of the undesired other materials to course hydrophobic interactions between the hydrophobized valuables and the hydrophobic magnetite. In a preferred embodiment, the at least one surface altering substance is added in an amount of from 5 g / t smelter slag to be separated to 1000 g / t smelter slag to be separated, particularly preferably from 50 g / t mixture to be separated to 200 g / t smelter slag to be separated, further preferably from 80 g / t mixture to be separated to 180 g / t smelter slag to be separated.

In general, the amount of at least one magnetic particle can be determined by a person having ordinary skill in the art in a way that advantageously the whole amount of at least one first material can be separated by agglomerating with the at least one magnetic particle. In a preferred embodiment of the process according to the present invention, the at least one magnetic particle is added in an amount of 0.01 to 6% by weight, preferably 0.05 to 4.5% by weight, particularly preferably 0.1 to 3 % by weight, in respect of the slag to be separated in each case.

The present invention therefore preferably relates to a process as mentioned above, wherein at least one magnetic particle is added in an amount of 0.1 to 3 % by weight, in respect the slag to be separated.

The positive effect which is connected with this specific amount of at least one magnetic particle that is preferably used, is that agglomerates which are obtained after step (D) of the process according to the present invention can preferably directly be transferred to further work-up steps, like smelting processes.

After step (A) or step (B) of the process according to the present invention a mixture is obtained comprising the further components of the slag and agglomerates of the at least one metal and the at least one magnetic particle, wherein the at least one surface altering substance is at least partly located between the at least one metal and the at least one magnetic particle, optionally in aqueous dispersion.

Step (C):

Optional step (C) comprises addition of at least one dispersant to the mixture obtained in step (A) or (B) to give a dispersion having a suitable concentration.

In one embodiment, if steps (A) and (B) are carried out in bulk, the mixture obtained after step (A) or (B) comprises the further components of the slag and particles or agglomerates of the at least one metal and the at least one magnetic particle, wherein, in one embodiment, the at least one surface altering substance is located between the at least one metal and the at least one magnetic particle. In this case, wherein steps (A) and (B) are carried out in bulk, step (C) of the process of the invention is preferably carried out, i.e. at least one suitable dispersion medium is added to the mixture obtained in step (B) in order to obtain a dispersion having a suitable concentration.

In the second possible and preferred embodiment according to the present invention in which steps (A) and/or (B) of the process of the invention are carried out in dispersion, step (C) does not have to be carried out. However, in this embodiment, too, it is possible to carry out step (C), i.e. to add further dispersion medium in order to obtain a dispersion having a lower concentration.

Suitable dispersion media are all dispersion media which have been mentioned above in respect of steps (A) and (B). In a particularly preferred embodiment, the dispersion medium in steps (A) and (B) is water. A particularly preferred dispersion medium which is added in step (C) of the process according to the present invention is water, optionally mixed with at least one polar organic solvent that have been mentioned in respect of step (A).

Thus, step (C) comprises either converting the mixture present in bulk from steps (A) and (B) into a dispersion or converting the mixture which is already in dispersion from steps (A) and/or (B) into a dispersion of lower concentration by addition of dispersion media.

According to the invention, the amount of dispersion medium added in step (A) and/or step (B) can generally be selected so that a dispersion which is readily stirrable and/or conveyable is obtained.

In a preferred embodiment, the amount of dispersion medium that is added in step (C) of the process according to the present invention is determined to obtain a dispersion having a solid content of 1 to 80 % by weight, preferably 10 to 45 % by weight, particularly preferably 30 to 40 % by weight, in each case based on the whole amount of solids that have to dispersed.

The addition of dispersion medium in step (C) of the process of the invention can, according to the invention, be carried out by all methods known to those skilled in the art.

Step (D):

Step (D) of the process of the invention comprises separation of the particles from the mixture of step (A) or of the agglomerates from the mixture of step (B) or (C) by application of a magnetic field.

In one embodiment of the process according to the present invention, step (D) comprises separation of the particles from the mixture of step (A) or (A1) respectively, by application of a magnetic field. In this embodiment, the slag that is to be treated comprises the at least one metal to be separated and magnetic substances like iron comprising oxides. The components are present in particles after step (A) or (A1) respectively.

In a second embodiment of the process according to the present invention, step (D) comprises separation of the agglomerates from the mixture of step (B) or (C) by application of a magnetic field. In this embodiment, the ground slag that obtained after step (A) is further treated in step (B) according to the present invention to obtain magnetic agglomerates.

In general, step (D) can be carried out with any magnetic equipment that is suitable to separate magnetic particles from dispersion, e. g. drum separators, high or low intensity magnetic separators, continuous belt type separators or others.

Step (D) can, in a preferred embodiment, be carried out by introducing a permanent magnet into the reactor in which the mixture of step (D) is present. In a preferred embodiment, a dividing wall composed of nonmagnetic material, for example the wall of the separator, is present between permanent magnet and mixture to be treated. In a preferred embodiment, step (D) is conducted in reactors that are covered at least partially with permanent magnets at the inside. These permanent magnets can be controlled mechanically. According to another embodiment, the addition of the mixture obtained in step (A), (A1), (B) or (C) is controlled mechanically.

In a preferred embodiment, the magnetic separation equipment allows to wash the magnetic concentrate while the separation with a dispersant, preferred water. This washing preferably allows removing inert material from the magnetic concentrate, which leads to higher grades of the valuables.

In a preferred embodiment, step (D) is conducted continuously or semi-continuously, wherein preferably the mixture to be treated flows through separator, preferably in dispersion. Flow velocities of the dispersion to be treated are in general adjusted to obtain an advantageous yield of magnetic agglomerates separated. In a preferred embodiment, flow velocities of the dispersion to be treated are 10 mm/sec. to 1000 mm/sec.

The pH-value of the dispersion which is treated according to step (D) is in general neutral or weakly basic, being a pH-value of about 6 to 8. In a preferred embodiment, no adjustment of pH-value of the dispersion obtained in step (A) or (B) is necessary.

Step (D) of the process of the invention can be carried out at any suitable temperature, for example from 10 to 60 °C, preferably at ambient temperature.

In a continuous or semi-continuous process the mixture is preferably mixed by turbulent flow, and is preferably not additionally stirred.

The magnetic agglomerates can be separated from the magnetic surface and/or the unit wherein magnetic separation is conducted according to the present invention by all methods known to those skilled in the art.

In a preferred embodiment the magnetic agglomerates are removed by flushing with a suitable dispersion medium. Suitable dispersion media have been mentioned above. In a preferred embodiment, water is used to flush the separated magnetic agglomerates.

The separated magnetic agglomerates can be dewatered and/or dried afterwards by processes known to those skilled in the art. The magnetic agglomerates are dewatered until a suitable solvent content, in particular water content, of preferably less than 30% by weight, is reached.

The process according to the present invention comprises steps (A) to (D), wherein particles or agglomerates are obtained comprising at least one magnetic particle and at least one metal. In a particularly preferred embodiment these particles or agglomerates are suitable for direct work-up to obtain the at least one metal in pure form.

The present invention further relates to the process according to the present invention, wherein after step (D) the following step (E) is conducted:

(E) further processing of the particles or of the agglomerate from step (D) via smelting, extracting and/or wet chemical refining.

The magnetic particles or agglomerates obtained in step (D) preferably comprise iron comprising magnetic substances or magnetic particles in addition to at least one metal, being preferably at least one precious metal. Because iron is essentially necessary for melting and/or smelting processes to obtain the at least one metal in pure form, the particles or agglomerates that are obtained in step (D) of the process according to the present invention can directly be treated in a smelting and/or melting process.

In the case that precious metals are used as first material in combination with iron comprising magnetic particles, no need for further addition of other iron containing compounds exists. Instead, the magnetic iron oxide particles loaded with precious metals are added to the furnace feed in place of iron oxide otherwise added to the process.

The present invention further relates to the process according to the present invention, wherein after step (D), the following step (F) is conducted:

(F) cleavage of the agglomerates from step (D) and, if appropriate, processing of the at least one metal via smelting, extracting and/or wet chemical refining..

Optional step (F) of the process according to the present invention is preferably conducted, if agglomerates are formed in step (B) due to hydrophobic interactions between the at least one metal and the at least one magnetic particle. Therefore, these agglomerates have to be cleaved in order to obtain the at least one metal which can then be further processed by smelting, melting and/or refining.

Cleavage of the agglomerates is preferably carried out in a destructive or nondestructive manner, preferably in a non-destructive manner i.e. the individual components present in the dispersion are not changed chemically.

Cleavage can preferably be carried out by all methods known to those skilled in the art which are suitable for cleaving the addition product in such a way that the at least one metal magnetic particle can be recovered in reusable form.

In a preferred embodiment, cleavage according to the present invention is affected by treatment of the addition product with a substance selected from the group consisting of organic solvents, basic compounds, acidic compounds, oxidants, reducing agents, surface-active compounds and mixtures thereof. In a preferred embodiment, the cleavage is made by the use of biodegradable surfactants with concentrations in the range of the critical micelle concentrations.

Optional smelting, melting and/or refining are conducted according to step (F) and/or processes that are known to the skilled artisan. In a preferred embodiment, smelting, extracting and/or refining is conducted in step (F).

In particular, in a first embodiment (alternative 1), the present invention preferably relates to the process according to the present invention, comprising at least the following steps:

(A) grinding the slag to obtain particles,

(C) if appropriate, addition of at least one dispersant to the mixture obtained in step (A) to give a dispersion having a suitable concentration, and

(D) separation of the particles from the mixture of step (A) or (C) by application of a magnetic field.

This preferred first embodiment of the process according to the present invention comprising process steps (A), optionally (C) and (D) is preferably conducted, if a slag is to be separated which is obtained by slow cooling and which is generated under reductive conditions.

In particular, in a second embodiment (alternative 2), the present invention preferably relates to the process according to the present invention, comprising at least the following steps:

(A) grinding the slag to obtain particles,

(A1) Addition of at least one dispersant to the mixture obtained in step (A) to give a dispersion having a suitable concentration,

(B) contacting the ground slag of step (A) with at least one magnetic particle, if appropriate in the presence of at least one dispersant, resulting in formation of agglomerates of the at least one metal and the at least one magnetic particle due to magnetic interactions,

(D) separation of the agglomerates from the mixture of step (B) or (C) by application of a magnetic field.

This preferred second embodiment of the process according to the present invention comprising process steps (A), (A1), (B) and (D) is preferably conducted, if a slag is to be separated which is obtained by rapidly (shock) cooled slags generated under reductive conditions.

In particular, in a third embodiment (alternative 3), the present invention preferably relates to the process according to the present invention, comprising at least the following steps:

(A) grinding the slag to obtain particles,

(B) contacting the ground slag of step (A) with at least one magnetic particle and at least one surface-altering substance, if appropriate in the presence of at least one dispersant, resulting in formation of agglomerates of the at least one metal and the at least one magnetic particle due to magnetic and hydrophobic interactions,

(C) if appropriate, addition of at least one dispersant to the mixture obtained in step (B) to give a dispersion having a suitable concentration, and

(D) separation of the agglomerates from the mixture of step (B) or (C) by application of a magnetic field.

This preferred third embodiment of the process according to the present invention comprising process steps (A), (B), optionally (C) and (D) is preferably conducted, if a slag is to be separated which is obtained by rapidly (shock) cooled slags generated under reductive conditions.

The present invention further relates to the use of at least one magnetic particle for the separation of slag, in particular for separating at least one metal from the slag.

In particular, the present invention relates to the use according to the present invention, wherein the at least one magnetic particle comprises iron or iron oxides.

General embodiments and preferred embodiments of slag, components present in the slag, metals to be separated and further conditions are mentioned above in respect of the process according to the present invention.

Examples

PGM is the abbreviation of Precious Group Metals, being Au, Pt, Ir, Pd, Os, Ag, Hg, Rh, Ru, in particular Au, Pt, Pd, Rh, further preferred Pt, Pd, Rh.

Example 1:

Example 1 is carried out using already hydrophobized magnetite, and the addition of a surface altering substance, which hydrophobizes the at least one metal, being valuables like Pd, Pt and Rh.

300 g electro furnace slag with the composition 27% by weight SiO_2, 26% by weight CaO, 34% by weight Al_2O_3, 4% by weight MgO, 3% by weight P_2O_5, 3% by weight ZrO_2, 2% by weight Fe_2O_3, 1% by weight CeO_2, > 1% by weight Cr_2O_3, 17 ppm Pt, 12 ppm Pt and 2.5 ppm Rh is milled for 60 min. in a ball mill in the presence of 300 ml water and 500 g of zirconia balls (1.7 - 2.2 mm in size). The material is sieved after milling via a 100 µm sieve. The fine fraction (particle size below 100 µm) is treated for another 5 min. with 100 g/t octyl xanthate and with 2 g / 100 g hydrophobic magnetite (E 8707 H, Lanxess). The slurry is mixed with water to a solid content of 20% by weight and is pumped through a high intensity filter and the magnetic compounds are removed magnetically.

After the separation, 2.66 g magnetic concentrate was produced with a concentration of 630 ppm Pt, 520 ppm Pd and 95 ppm Rh, the yield is calculated with Pt: 95.6 %, Pd: 78,0 %, Rh: < 99 %.

Example 2:

Example 2 is carried out using not hydrophobized magnetite and without a surface altering substance to separate the at least one metal, being valuables like Pd, Pt and Rh.

100 g electro furnace slag with the composition 27% by weight SiO_2, 26% by weight CaO, 34% by weight Al_2O_3, 4% by weight MgO, 3% by weight P_2O_5, 3% by weight ZrO_2, 2% by weight Fe_2O_3, 1% by weight CeO_2, > 1% by weight Cr_2O_3, 17 ppm Pt, 12 ppm Pt and 2.5 ppm Rh is milled for 60 min. in a ball mill in the presence of 300 ml water and 500 g of zirconia balls (1.7 - 2.2 mm in size). The material is sieved after milling via a 100 µm sieve. The fine fraction (particle size below 100 µm) is treated with 1 g / 100 g non hydrophobic magnetite (E 8706, Lanxess). The slurry is mixed with water to a solid content of 20% by weight and the magnetic compounds are removed magnetically.

After the separation, 1.67 g magnetic concentrate was produced with a concentration of 303 ppm Pt, 394.5 ppm Pd and 76 ppm Rh, the yield is calculated with Pt: 48,4 %, Pd: 40,3 %, Rh: 48,4 %.

Example 3:

The process according to example 3 is carried out neither using additional magnetite nor additional surface altering substance.

100 g electro furnace slag with the composition 27% by weight SiO_2, 26% by weight CaO, 34% by weight Al_2O_3, 4% by weight MgO, 3% by weight P_2O_5, 3% by weight ZrO_2, 2% by weight Fe_2O_3, 1% by weight CeO_2, > 1% by weight Cr_2O_3, 17 ppm Pt, 12 ppm Pt and 2.5 ppm Rh is milled for 60 min. in a ball mill in the presence of 300 ml water and 500 g of zirconia balls (1.7 - 2.2 mm in size). The material is sieved after milling via a 100 µm sieve. The fine fraction (particle size below 100 µm) is mixed with water to a solid content of 20% by weight and the magnetic compounds are removed magnetically.

After the separation, 1.67 g magnetic concentrate was produced with a concentration of 1880 ppm Pt, 2270 ppm Pd and 390 ppm Rh, the yield is calculated with Pt: 14 %, Pd: 18 %, Rh: 17 %.

Example 4:

The process according to example 3 is carried out neither using additional magnetite nor additional surface altering.

300 g electro furnace slag is used. This electro furnace slag contains 30 to 40 % SiO_2, 30 to 40 % Al_2O_3 and / or other metal oxides. The slag contains less than 5 % sulphides. Further, 1,1 % Fe and 0,1 % Ni are present and 22 ppm Pt, 22 ppm Pd, 5 ppm Rh and 0.15 ppm Au. Pt, Pd, Rh and Au are summarized as the precious group metals (PGMs).

The slag is ground with a stirred ball mill to a d_{80} = 130 µm and suspended in water (20% solids in water). The slurry is treated with a magnetic separation equipment which can especially separate fine particles and very weak magnetic particles. After the separation, 61 to 64 % of the PGMs can be recovered in the magnetic fraction with a grade of 58 oz/t.

Example 5:

The process according to example 3 is carried out neither using additional magnetite nor additional surface altering.

300 g electro furnace slag is used. This electro furnace slag contains 30 to 40 % SiO_2, 30 to 40 % Al_2O_3 and / or other metal oxides. The slag contains less than 5 % sulphides. Further, 1,1 % Fe and 0,1 % Ni are present and 22 ppm Pt, 22 ppm Pd, 5 ppm Rh and 0.15 ppm Au. Pt, Pd, Rh and Au are summarized as the precious group metals (PGMs).

The slag is ground with a stirred ball mill to a d_{80} = 9 µm and suspended in water (20 % solids in water). The slurry is treated with a magnetic separation equipment which can especially separate fine particles and very weak magnetic particles. After the separation, 68 to 72 % of the PGMs can be recovered in the magnetic fraction with a grade of 144 oz/t.

Example 6:

Example 6 is carried out using hydrophobized magnetite and a surface altering substance to separate the at least one metal, being valuables like Pd, Pt and Rh.

300 g electro furnace slag is used. This electro furnace slag contains 30 to 40 % SiO_2, 30 to 40 % Al_2O_3 and / or other metal oxides. The slag contains less than 5 % sulphides. Further, 1,1 % Fe and 0,1 % Ni are present and 22 ppm Pt, 22 ppm Pd, 5 ppm Rh and 0.15 ppm Au. Pt, Pd, Rh and Au are summarized as the precious group metals (PGMs).

The slag is ground with a stirred ball mill to a d_{80} = 9 µm and suspended in water (20 % solids in water). In addition 0.5 g per 100 g slag hydrophobized magnetite is added (E 8707, Lanxess) and 100 g/t Amyl Xanthate (99 %, Aldrich). Sufficient shear energy is introduced to combine the hydrophobic magnetite and the surface altering substance and the PGM containing particles. Afterwards, the slurry is treated with a magnetic separation equipment which can especially separate fine particles and very weak magnetic particles. After the separation, 77 to 82 % of the PGMs can be recovered in the magnetic fraction with a grade of 60 oz/t.

Example 7: Pure magnetic separation of slag (steps A + C + D of the process according to the present invention) with shock cooled slag

The slag has the composition of 28 % SiO_2, 26 % CaO, 35 % Al_2O_3, 4 % MgO, 3 % P_2O_5, 3 % ZrO_2, 2 % Fe_2O_3 (or other Fe-O species like Fe_3O_4), 1 % CeO_2, 12 ppm Pt, 17 ppm Pd, 2.5 ppm Rh. The slag has been shock cooled that means the hot slag has been introduced into a concrete vessel with water. 300 g of this material is milled for 60 min. in a ball mill in the presence of 300 ml water and 500 g of zirconia balls (1.7 - 2.2 mm in size). The material is sieved after milling via a 100 µm sieve. The fine fraction (d_{80} = 9 µm) is treated via the embodiment of the process described only with the step A (grinding, as already described), C (addition of a dispersant, in this case water to a solid content between 15 weight-%) and D (magnetic separation).

36 % of the Pt, 56 % of the Pd and 12 % of the Rh could be recovered magnetically with an overall grade of 1577 ppm PGMs.

Example 8: Assisted magnetic separation of slag (steps A + A1 + B + D of the process according to the present invention) with shock cooled slag

The slag has the composition of 28 % SiO_2, 26 % CaO, 35 % Al_2O_3, 4 % MgO, 3 % P_2O_5, 3 % ZrO_2, 2 % Fe_2O_3 (or other Fe-O species like Fe_3O_4), 1 % CeO_2, 12 ppm Pt, 17 ppm Pd, 2.5 ppm Rh.

The slag has been shock cooled that means the hot slag has been introduced into a concrete vessel with water.

300 g of this material is milled for 60 min. in a ball mill in the presence of 300 ml water and 500 g of zirconia balls (1.7 - 2.2 mm in size). The material is sieved after milling via a 100 µm sieve. The fine fraction (d_{80} = 9 µm) is treated via the embodiment of the process described with the step A (grinding, as already described), A1 (addition of a dispersant, in this case water to a solid content between 15 weight-%), the step B (addition of non surface modified magnetite, in this case 3 g / 100 g E 8706 (Lanxess)) and D (magnetic separation). The addition of the non surface modified magnetite can be done within the mill (stirred ball mill, ball mill, verti mill or others) or with a t-tube or with other possible equipments which ensure a good mixing and the input of some shear.

44 % of the Pt, 63 % of the Pd and 69 % of the Rh could be recovered magnetically with an overall grade of 330 ppm PGMs. The non surface modified magnetite will not

be removed from the PGM containing concentrate which causes the reduction of the grade.

Example 9: Assisted magnetic separation of slag (steps A + A1 + B + D of the process according to the present invention) with shock cooled slag

The slag has the composition of 28 % SiO_2, 26 % CaO, 35 % Al_2O_3, 4 % MgO, 3 % P_2O_5, 3 % ZrO_2, 2 % Fe_2O_3 (or other Fe-O species like Fe_3O_4), 1 % CeO_2, 12 ppm Pt, 17 ppm Pd, 2.5 ppm Rh.

The slag has been shock cooled that means the hot slag has been introduced into a concrete vessel with water.

300 g of this material is milled for 60 min. in a ball mill in the presence of 300 ml water and 500 g of zirconia balls (1.7 - 2.2 mm in size). The material is sieved after milling via a 100 µm sieve. The fine fraction (d_{80} = 9 µm) is treated via the embodiment of the process described with the step A (grinding, as already described), A1 (addition of a dispersant, in this case water to a solid content between 15 weight-%), the step B (addition of a collector which hydrophizes selectively the valuables in the presence of the undesired other oxides, in this case 650 g/t C_8-xanthate (BASF R & D sample) and hydrophobic magnetite (E 8707H, magnetite hydrophobized with silicon oil, Lanxess), 3 g hydrophobic magnetite / 100 g slag and D (magnetic separation). The addition of the collector and the hydrophobic magnetite can be done within the mill (stirred ball mill, ball mill, verti mill or others) or with a t-tube or with other possible equipments which ensure a good mixing and the input of some shear. For an optimal dispersion of the hydrophobic magnetite, 0.01 % Lutensol XL 80 was added as a surfactant.

83 % of the Pt, 88 % of the Pd and 88 % of the Rh could be recovered magnetically with an overall grade of 1362 ppm PGMs. The magnetite will not be removed from the PGM containing concentrate which causes the reduction of the grade. However, the magnetic material was washed via flushing after the magnetic separation step and with that the grade could be increased.

Example 10: Magnetic separation of slag (steps A + C + D of the process according to the present invention) with slowly cooled slag

The slag has the composition of 28 % SiO_2, 26 % CaO, 35 % Al_2O_3, 4 % MgO, 3 % P_2O_5, 3 % ZrO_2, 2 % Fe_2O_3 (or other Fe-O species like Fe_3O_4), 1 % CeO_2, 12 ppm Pt, 17 ppm Pd, 2.5 ppm Rh.

The slag has been slowly cooled down to RT by exposing the slag several days to RT.

300 g of this material is milled for 60 min. in a ball mill in the presence of 300 ml water and 500 g of zirconia balls (10 mm in size). The material is sieved after milling via a 100 µm sieve. The fine fraction (d_{80} = 9 µm) is treated via the embodiment of the process described only with the step A (grinding, as already described), C (addition of a dispersant, in this case water to a solid content between 15 weight-%) and D (magnetic separation). 78 % of the Pt, 77 % of the Pd and 79 % of the Rh could be recovered magnetically with an overall grade of 2333 ppm PGMs.

Example 11: Assisted magnetic separation of slag (steps A + A1 + B + D of the process according to the present invention) with slowly cooled slag

300 g of this material is milled for 60 min. in a ball mill in the presence of 300 ml water and 500 g of zirconia balls (1.7 - 2.2 mm in size). The material is sieved after milling via a 100 µm sieve. The fine fraction (d_{80} = 9 µm) is treated via the embodiment of the process described with the step A (grinding, as already described), A1 (addition of a dispersant, in this case water to a solid content between 15 weight-%), the step B (addition of a collector which hydrophizes selectively the valuables in the presence of the undesired other oxides, in this case 100 g/t C_8-xanthate (BASF R & D sample) and hydrophobic magnetite (E 8707H, magnetite hydrophobized with silicon oil, Lanxess), 1 g hydrophobic magnetite / 100 g slag and D (magnetic separation). The addition of the collector and the hydrophobic magnetite can be done within the mill (stirred ball mill, ball mill, verti mill or others) or with a t-tube or with other possible equipments which ensure a good mixing and the input of some shear. For an optimal dispersion of the hydrophobic magnetite, 0.01 % Lutensol XL 80 was added as a surfactant.

83 % of the Pt, 83 % of the Pd and 86 % of the Rh could be recovered magnetically with an overall grade of 1506 ppm PGMs. The magnetite will not be removed from the PGM containing concentrate which causes the reduction of the grade. However, the magnetic material was washed via flushing after the magnetic separation step and with that the grade could be increased.

Claims

1. Process for the separation of at least one metal from a slag, comprising that at least one metal and further components, comprising at least the following steps:

   (A) grinding the slag to obtain particles,

   (B) if appropriate, contacting the ground slag of step (A) with at least one magnetic particle and/or at least one surface altering substance, if appropriate in the presence of at least one dispersant, resulting in formation of agglomerates of the at least one metal and the at least one magnetic particle due to magnetic and/or hydrophobic interactions,

   (C) if appropriate, addition of at least one dispersant to the mixture obtained in step (A) or (B) to give a dispersion having a suitable concentration, and

   (D) separation of the particles from the mixture of step (A) or of the agglomerates from the mixture of step (B) or (C) by application of a magnetic field.

2. Process according to claim 1, wherein after step (D) the following step (E) is conducted:

   (E) further processing of the particles or the agglomerates from step (D) via smelting, extracting and/or wet chemical refining.

3. Process according to claim 1, wherein after step (D), the following step (F) is conducted:

   (F) cleavage of the agglomerates from step (D) and, if appropriate, processing of the at least one metal via smelting, extracting and/or wet chemical refining.

4. Process according to any of claims 1 to 3, wherein the at least one metal is selected from the group consisting of Ag, Au, Pt, Pd, Rh, Ru, Ir, Os, Cu, Mo, Ni, Mn, Zn, Pb, Te, Sn, Hg, Re, V, Fe and mixtures thereof.

5. Process according to any of claims 1 to 4, wherein the slag that is introduced into claim (A) is an artificially prepared slag.

6. Process according to any of claims 1 to 5, wherein the slag comprises at least one compound selected from the group consisting of SiO_2, CaO, Al_2O_3, MgO, P_2O_3, ZrO_2, Fe_2O_3, Fe_3O_4, CeO_2, Cr_2O_3, complex oxide matrices and mixtures thereof.

7. Process according to any of claims 1 to 6, wherein, if step (B) is conducted, at least one magnetic particle is added in step (B) in an amount of 0.1 to 3 % by weight, in respect of the slag to be separated.

8. Process according to any of claims 1 to 7, wherein the at least one metal is present in the slag in an amount of 0.01 to 1000 g/t of slag to be separated.

9. Process according to any of claims 1 to 8, wherein the at least one magnetic particle is an iron-comprising compound.

10. Process according to any of claims 1 to 9, wherein after step (A) step (A1) is conducted, comprising

    (A1) Addition of at least one dispersant to the mixture obtained in step (A) to give a dispersion having a suitable concentration.

11. The use of at least one magnetic particle for the separation of slag.

12. The use according to claim 11, wherein the at least one magnetic particle comprises iron or iron oxides.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2011/071244

A. CLASSIFICATION OF SUBJECT MATTER
INV. B03C1/01
ADD.

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)
B03C

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 practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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

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"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

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Date of the actual completion of the international search 20 March 2012	Date of mailing of the international search report 28/03/2012
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 Menck, Anja

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2011/071244

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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