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(54) **MAGNETIC SEPARATION OF PARTICLES INCLUDING ONE-STEP-CONDITIONING OF A PULP**

MAGNETISCHE TRENNUNG VON PARTIKELN MIT EINER IN EINEM SCHRITT ERFOLGENDEN AUFBEREITUNG EINER PULPE

SÉPARATION MAGNÉTIQUE DE PARTICULES COMPRENANT UN TRAITEMENT EN UNE ÉTAPE D'UNE PÂTE

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(56) References cited:

WO-A1-2011/058039 WO-A1-2012/072615
US-A1- 2011 240 527

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Description

[0001] The present invention 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 by contacting said mixture with at least one magnetic particle and at least one surface-modifying substance at the same time, so that the at least one first material, the at least one surface-modifying substance and the at least one magnetic particle become attached to one another, and by subsequently separating the addition product from the mixture by application of a magnetic field.

[0002] In particular, the present invention relates to a process for the enrichment of ores in the presence of the gangue.

[0003] Processes for separating ores from mixtures comprising these are already known from the prior art.

[0004] 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.

[0005] 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 hydrophobized 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. Furthermore, in this process only C₄-hydrophobising agents are used for the ore.

[0006] US 4,834,898 discloses a process for separating off nonmagnetic materials by bringing them into contact with magnetic reagents which are enveloped by two layers of surface-modifying substances. US 4,834,898 also discloses that the surface charge of the nonmagnetic particles which are to be separated off can be influenced by various types and concentrations of electrolytes reagents. For example, the surface charge is altered by addition of multivalent anions, for example tripolyphosphate ions.

[0007] S. R. Gray, D. Landberg, N. B. Gray, Extractive Metallurgy Conference, Perth, 2 - 4 October 1991, pages 223 - 226, disclose a process for recovering small gold particles by bringing the particles into contact with magnetite. Before contacting, the gold particles are treated with potassium amylxanthogenate. A process for separating the gold particles from at least one hydrophilic material is not disclosed in this document.

[0008] WO 2007/008322 A1 discloses a magnetic particle which is hydrophobized on the surface for separating impurities from mineral substances by magnetic separation processes. According to WO 2007/008322 A1, a dispersant selected from among sodium silicate, sodium polyacrylate and sodium hexametaphosphate can be added to the solution or dispersion.

[0009] US 2011/240527 A1 and WO 2011/058039 A1 disclose processes for separating at least one first material from a mixture comprising this at least one first material and at least one second material by contacting said mixture with at least one magnetic particle and at least one surface-modifying substance in consecutive steps, so that the at least one first material, the at least one surface-modifying substance and the at least one magnetic particle become attached to one another, and by subsequently separating the addition product from the mixture by application of a magnetic field. WO2009/030669 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 first material is firstly brought into contact with a surface-modifying substance to hydrophobize it, this mixture is then brought into contact with at least one magnetic particle so that the magnetic particle and the hydrophobized first material become attached to one another and this agglomerate is separated from the at least one second material by application of a magnetic field. 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. This document does not disclose that the addition of magnetic particles prior to a surface-modifying substance or the addition of magnetic particles and a surface-modifying substance at the same time gives rise to certain advantages like accelerated agglomeration.

[0010] It is an object of the present invention to provide a process by means of which at least one first material can be efficiently separated from mixtures comprising at least one first material and at least one second material. A further object of the present invention is to treat the first particles to be separated off in such a way that the addition product of magnetic particle and first material is sufficiently stable to ensure a high yield of the first material in the separation.

[0011] A further object is to provide a process for separating particles from a mixture comprising them and other particles, using magnetic particles to obtain magnetic agglomerates of particles to be separated and magnetic particles, wherein the agglomeration occurs faster and more evenly than in processes of the prior art.

[0012] These objects are achieved by a process as defined in claim 1 for separating at least one first material from a

mixture comprising this at least one first material and at least one second material, which comprises the following steps:

(A) contacting of the mixture comprising at least one first material and at least one second material with at least one magnetic particle and at least one surface-modifying substance at the same time, so that the at least one first material, the at least one surface-modifying substance and the at least one magnetic particle become attached to one another, if appropriate in the presence of at least one dispersant,

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

(C) separation of the addition product from step (A) or (B) from the mixture by application of a magnetic field,

(D) if appropriate, cleavage of the addition product which has been separated off in step (C) to obtain the at least one first material and the at least one magnetic particle separately.

[0013] The process of the invention is employed for separating at least one first, hydrophobic material from a mixture comprising this at least one first, hydrophobic material and at least one second, hydrophilic material.

[0014] For the purposes of the present invention, "hydrophobic" means that the corresponding particle can subsequently be hydrophobized by treatment with the at least one surface-modifying substance.

[0015] It is also possible for a particle which is hydrophobic per se to be additionally hydrophobized by treatment with the at least one surface-modifying substance.

[0016] Within the scope of the present invention, "hydrophobic" means that the surface of corresponding "hydrophobic substances", and, respectively, of a "hydrophobized substance" has a contact angle with water against air of $> 90^\circ$. In the scope of the present invention, "hydrophilic" means that the surface of corresponding "hydrophilic substance" has a contact angle with water against air of $< 90^\circ$.

[0017] In the process of the invention, the at least one first material is at least one hydrophobic metal compound or coal and the at least one second material is preferably at least one hydrophilic metal compound.

[0018] In the process according to the present invention, the at least one hydrophobic metal compound is selected from the group consisting of sulfidic ores, oxidic ores, carbonate-comprising ores, noble metals in elemental form, compounds comprising noble metals and mixtures thereof.

[0019] The present invention therefore relates to the process according to the present invention, wherein the at least one hydrophobic metal compound is selected from the group consisting of sulfidic ores, oxidic ores, carbonate-comprising ores, noble metals in elemental form, compounds comprising noble metals and mixtures thereof.

[0020] In the process according to the present invention, the at least one hydrophilic metal compound is selected from the group consisting of oxidic metal compounds, hydroxidic metal compounds and mixtures thereof.

[0021] The present invention therefore relates to the process according to the present invention, wherein the at least one hydrophilic metal compound is selected from the group consisting of oxidic metal compounds, hydroxidic metal compounds and mixtures thereof.

[0022] Examples of the at least one first material to be separated off are preferably metal compounds selected from the group consisting of sulfidic ores, oxidic and/or carbonate-comprising ores, for example azurite $[\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2]$ or malachite $[\text{Cu}_2[(\text{OH})_2]\text{CO}_3]$, rare earth metals comprising ores like bastnaesite $(\text{Y, Ce, La})\text{CO}_3\text{F}$, monazite $(\text{RE})\text{PO}_4$ (RE = rare earth metal) or chrysocolla $(\text{Cu, Al})_2\text{H}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot n\text{H}_2\text{O}$, noble metals in elemental form and their compounds to which a surface-modifying compound can become selectively attached to produce hydrophobic surface properties. Examples of noble metals that may be present as at least first material are Au, Pt, Pd, Rh, etc., preferably in the native state or as sulphides, phosphides, selenides, tellurides or as alloys with bismuth, antimony and/or other metals.

[0023] Examples of sulfidic ores which can be separated according to the invention are, for example, selected from the group of copper ores consisting of covellite CuS , molybdenum(IV) sulfide, chalcopyrite (cupriferous pyrite) CuFeS_2 , bornite Cu_5FeS_4 , chalcocite (copper glass) Cu_2S , pendlandite $(\text{Fe, Ni})_9\text{S}_8$, and mixtures thereof.

[0024] Suitable oxidic metal compounds which may be present as at least one second material according to the invention are preferably selected from the group consisting of silicon dioxide SiO_2 , silicates, aluminosilicates, for example feldspars, for example albite $\text{Na}(\text{Si}_3\text{Al})\text{O}_8$, mica, for example muscovite $\text{KAl}_2[(\text{OH, F})_2\text{AlSi}_3\text{O}_{10}]$, garnets $(\text{Mg, Ca, Fe}^{\text{II}})_3(\text{Al, Fe}^{\text{III}})_2(\text{SiO}_4)_3$ and further related minerals and mixtures thereof.

[0025] Accordingly, untreated ore mixtures obtained from mines are preferably used as mixture comprising at least one first material and at least one second material in the process of the invention.

[0026] In a preferred embodiment of the process of the invention, the mixture comprising at least one first material and at least one second material in step (A) is in the form of particles having a size of from 100 nm to 100 μm , see for example US 5,051,199. In a preferred embodiment, this particle size is obtained by milling. Suitable processes and apparatuses are known to those skilled in the art, for example wet milling in a ball mill. The mixture comprising at least

one first material and at least one second material is therefore milled to particles having a size of from 100 nm to 100 μm before or during step (A) in a preferred embodiment of the process of the invention. Preferred ore mixtures have a content of sulfidic minerals of at least 0.4% by weight, particularly preferably at least 10% by weight.

[0027] Examples of sulfidic minerals which are present in the mixtures which can be used according to the invention are those mentioned above. In addition, sulfide of metals other than copper, for example, sulfides of iron, lead, zinc or molybdenum, i.e. FeS , FeS_2 , PbS , ZnS or MoS_2 , can also be present in the mixtures. Furthermore, oxidic compounds of metals and semimetals, for example silicates or borates or other salts of metals and semimetals, for example phosphates, sulfates or oxides/hydroxides/carbonates, and further salts, for example azurite $[\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2]$, malachite $[\text{Cu}_2[(\text{OH})_2(\text{CO}_3)]]$, barite (BaSO_4), monazite $((\text{La-Lu})\text{PO}_4)$, spinels (Mg , Ca , Fe(II))(Fe(III)), Al , $\text{Cr})_2\text{O}_4$, can be present in the ore mixtures to be treated according to the invention.

[0028] A typical ore mixture which can be separated by means of the process of the invention has the following composition: about 30% by weight of SiO_2 as an example of a preferred at least one second material, about 30% by weight of feldspar (e.g. $\text{Na}(\text{Si}_3\text{Al})\text{O}_8$), about 3% by weight of CuFeS_2 as an example of a preferred at least one first material, about 0,05% by weight of MoS_2 , balance chromium, iron, titanium and magnesium oxides.

[0029] The individual steps of the process of the invention are described in detail below:

Step (A):

[0030] Step (A) of the process can be conducted according to two alternative embodiments, the first embodiment of which is not covered by the claimed invention. According to the first embodiment of the process not covered by the claimed invention, step (A) comprises contacting of the mixture comprising at least one first material and at least one second material with at least one magnetic particle, if appropriate in the presence of at least one dispersant.

[0031] According to this first embodiment only at least one magnetic particle is added in step (A), and at least one surface-modifying substance is added in step (C) of the process not covered by the claimed invention.

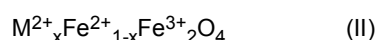
[0032] According to the second embodiment of the process according to the present invention, step (A) comprises contacting of the mixture comprising at least one first material and at least one second material with at least one magnetic particle and at least one surface-modifying substance at the same time, so that the at least one first material, the at least one surface-modifying substance and the at least one magnetic particle become attached to one another, if appropriate in the presence of at least one dispersant. According to this second embodiment, both, at least one magnetic particle and at least one surface active substance are added in step (A). According to this embodiment, step (C) of the process according to the present invention is not necessary and is preferably not conducted.

[0033] Suitable preferred first and second materials have been mentioned above.

[0034] According to the present invention at least one magnetic particle is added in step (A).

[0035] In a preferred embodiment of the process according to the present invention, at least one hydrophobic magnetic particle is added in step (A). In a preferred embodiment of the present invention, the at least one magnetic particle is hydrophobized at the surface.

[0036] In step (A) of the process of the invention, it is in general possible to use all magnetic substances and materials known to those skilled in the art. In a preferred embodiment, the at least one magnetic particle is selected from the group consisting of magnetic metals, for example iron, cobalt, nickel and mixtures thereof, ferromagnetic alloys of magnetic metals, for example NdFeB , SmCo and mixtures thereof, magnetic iron oxides, for example magnetite, maghemite, cubic ferrites of the general formula (II)



where

M is selected from among Co, Ni, Mn, Zn and mixtures thereof and

x is ≤ 1 ,

hexagonal ferrites, for example barium or strontium ferrite $\text{MFe}_6\text{O}_{19}$ where M = Ca, Sr, Ba, or a mixture thereof. The magnetic particles can additionally have an outer layer, for example of SiO_2 .

[0037] In a particularly preferred embodiment of the present invention, the at least one magnetic particle is magnetite or cobalt ferrite $\text{Co}^{2+}_x\text{Fe}^{2+}_{1-x}\text{Fe}^{3+}_2\text{O}_4$ where $x \leq 1$. Very preferably magnetite is used as at least one magnetic particle.

[0038] In a further preferred embodiment, in step (A) of the process according to the present invention, magnetic particles are present in the size of 100 nm to 100 μm , particularly preferred 1 to 50 μm . The magnetic particles may be brought into the adequate size by processes known to the skilled artisan, for example by milling. Furthermore, the particles, obtained from precipitation reaction, can be brought to the adequate particle size by setting up the reaction parameters (for example pH, reaction time, temperature).

[0039] In a further preferred embodiment, the at least one magnetic particle is hydrophobized at the surface by at least one hydrophobic compound. The hydrophobic compound is preferably selected from among compounds of the general formula (III)

5 B-Y (III),

where

10 B is selected from among linear or branched C₃-C₃₀-alkyl, C₃-C₃₀-heteroalkyl, optionally substituted C₆-C₃₀-aryl, optionally substituted C₆-C₃₀-heteroaryl, C₆-C₃₀-aralkyl, and
Y is a group by means of which the compound of the general formula (III) binds to the at least one magnetic particle.

15 **[0040]** In a particularly preferred embodiment, B is a linear or branched C₆-C₁₈-alkyl, preferably linear C₈-C₁₂-alkyl, very particularly preferably a linear C₁₂-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.

[0041] In a further particularly preferred embodiment, Y is selected from the group consisting of -(X)_n-SiHal₃, -(X)_n-SiHHal₂, -(X)_n-SiH₂Hal where Hal is F, Cl, Br, I, -(X)_n-Si(OR¹)_{3-n} wherein n is 1, 2 or 3 and R¹ is C₁-C₆-alkyl, and anionic groups such as -(X)_n-SiO₃³⁻, -(X)_n-CO₂⁻, -(X)_n-PO₃²⁻, -(X)_n-PO₂S²⁻, -(X)_n-POS₂²⁻, -(X)_n-PS₃²⁻, -(X)_n-PS₂⁻, -(X)_n-POS⁻, -(X)_n-PO₂⁻, -(X)_n-CO₂⁻, -(X)_n-CS₂⁻, -(X)_n-COS⁻, -(X)_n-C(S)NHOH, -(X)_n-S⁻ where X = O, S, NH, CH₂ and n = 20 0, 1 or 2, and, if appropriate, cations selected from the group consisting of hydrogen, NR₄⁺ where the radicals R are each, independently of one another, hydrogen or C₁-C₈-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.

[0042] If, in the mentioned formulas n = 2, two equal or different, preferably equal, groups B are attached to one group Y.

25 **[0043]** Very preferred hydrophobizing substances of general formula (III) are alkyltri-chlorosilane (alkyl group having 1 to 12 carbon atoms), alkyldialkoxysilane (alkyl group having 1 to 12 carbon atoms and alkoxy group having 1 to 6 carbon atoms), for example alkyldimethoxysilane (alkyl group having 1 to 12 carbon atoms), alkyltrialkoxysilane (alkyl group having 1 to 12 carbon atoms and alkoxy group having 1 to 6 carbon atoms), for example alkyltrimethoxysilane (alkyl group having 6 to 12 carbon atoms), octylphosphonic acid, lauric acid, oleic acid, stearic acid or mixtures thereof. Using alkyltrialkoxysilanes as hydrophobizing substances of general formula (III), preferably a polymeric hydrophobic layer is obtained at the surface of the magnetic particle.

30 **[0044]** The at least one magnetic particle is in general added in an amount that is high enough to have the complete amount of at least one first material embedded in agglomerates, preferably the at least one magnetic particle is added in excess. For example, the at least one magnetic particle is added in an amount of 0.1 to 20% by weight, preferably 0.5 to 5% by weight, in each case based on the amount of the complete mixture to be treated with the process according to the present invention.

35 **[0045]** According to the second embodiment of step (A) of the process according to the present invention, at least one surface-modifying substance is added. In general, all surface-modifying substances can be used according to the present invention that are able to modify the surface of the at least one first material in a way that agglomeration with at least one magnetic particle is possible.

40 **[0046]** For the purposes of the present invention, a "surface-modifying substance" is a substance which is able to modify the surface of the particle to be separated off in the presence of the other particles which are not to be separated off in such a way that attachment of a hydrophobic particle by means of hydrophobic interactions occurs. Surface-modifying substances which can be used according to the invention become attached to the at least one first material and thereby produce a suitable hydrophobicity of the first material.

45 **[0047]** In the process of the invention, preference is given to using a surface-modifying substance of the general formula (I)

A-Z (I)

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

A is selected from among linear or branched C₂-C₃₀-alkyl, C₂-C₃₀-heteroalkyl, optionally substituted C₆-C₃₀-aryl, optionally substituted C₆-C₃₀-heteroaryl, C₆-C₃₀-aralkyl, and

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

[0048] In a particularly preferred embodiment, A is a linear or branched C₂-C₁₄-alkyl, very particularly preferably a linear C₄- or C₈-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.

[0049] In a further preferred embodiment, A is preferably a branched, C₂-C₂₀-alkyl, particularly preferably a branched C₆-C₁₄-alkyl, wherein preferably the at least one substituent, preferably having 1 to 6 carbon atoms, is attached in 2-position, for example 2-ethylhexyl and/or 2-propylheptyl. Corresponding compounds being substituted in 2-position are,

for example, obtained using the Guerbet reaction that is known to the skilled artisan as one reaction step.

[0050] 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, CH₂ and n = 0, 1 or 2, with, if appropriate, cations selected from the group consisting of hydrogen, NR₄⁺ with R being independently of one another hydrogen and/or C₁-C₈-alkyl, hydroxy-substituted C₁-C₈-alkyl or -heteroalkyl, like 2-hydroxy-ethyl HO-CH₂CH₂- or 2-hydroxy-ethoxy-ethyl HO-CH₂CH₂-O-CH₂CH₂-, alkali- or earth alkali metals, preferably sodium or potassium, are present. The anions mentioned and the corresponding cations form, according to the invention, uncharged compounds of the general formula (I).

[0051] If, in the mentioned formulas n = 2, two equal or different, preferably equal, groups A are attached to one group Z.

[0052] In a further preferred embodiment, compounds are applied, selected from the group consisting of xanthates A-O-CS₂-, dialkyldithiophosphates (A-O)₂-PS₂-, dialkyldithio-phosphinates (A)₂-PS₂-, dialkyldithiocarbamates, alkyltrithiocarbamates, dithiophosphates and mixtures thereof, wherein A independently of one another is a linear or branched, preferably linear, C₆-C₂₀-alkyl, for example n-octyl, or a branched C₆-C₁₄-alkyl, wherein the branch is preferably located in 2-position, for example 2-ethylhexyl and/or 2-propylheptyl. As counterions, in these compounds preferably cations selected from the group consisting of hydrogen, NR₄⁺ with R being independently of one another hydrogen and/or C₁-C₈-alkyl, hydroxy-substituted C₁-C₈-alkyl or -heteroalkyl, like 2-hydroxy-ethyl HO-CH₂CH₂- or 2-hydroxy-ethoxy-ethyl HO-CH₂CH₂-O-CH₂CH₂-, alkali- or earth alkali metals, preferably sodium or potassium, are present.

[0053] Exceptionally preferred compounds of general formula (I) are selected from the group consisting of sodium- or potassium-n-octylxanthate, sodium- or potassium-butylxanthate, sodium- or potassium-di-n-octyldithiophosphate, sodium- or potassium-di-n-octyldithiocarbamates and mixtures of these compounds.

[0054] In the case of noble metals, for example Au, Pd, Rh, etc., particularly preferred surface-modifying substances are monothiols, dithiols and trithiols, or 8-hydroxyquinolines, for example as described in EP 1200408 B1.

[0055] In the case of metal oxides, for example FeO(OH), Fe₃O₄, ZnO, etc., carbonates, for example azurite [Cu(CO₃)₂(OH)₂], malachite [Cu₂[(OH)₂CO₃]], particularly preferred surface-modifying substances are octylphosphonic acid (OPS), (EtO)₃Si-A, (MeO)₃Si-A, with the abovementioned meanings of A.

[0056] In the case of metal sulfides, for example Cu₂S, MoS₂, FeS₂ etc., particularly preferred surface-modifying substances are monothiols, dithiols and trithiols, xanthogenates or dithiophosphates.

[0057] Therefore, according to the above mentioned, in a further preferred embodiment of the process of the invention, Z is $-(X)_n-CS_2^{-}$, $-(X)_n-PS_2^{-}$ or $-(X)_n-S^{-}$ where X is O and n is 0 or 1, and a cation is selected from among hydrogen, sodium, potassium and NH_x(CH₂CH₂OH)_{4-x}, wherein x is 0, 1, 2, 3, or 4.

[0058] The at least one surface-modifying substance is generally used in an amount which is sufficient to achieve the desired effect. In a preferred embodiment, the at least one surface-modifying substance is added in an amount of from 0.001 to 1% by weight, preferably 0.001 to 0.1% by weight in each case based on the total mixture to be treated.

[0059] According to the first embodiment of step (A) of the process which is not covered by the claimed invention, the contacting of the mixture with at least one magnetic particle in step (A) of the process of the invention can be carried out by all methods known to those skilled in the art, for example in bulk or in dispersion, preferably in suspension. In a preferred first embodiment not covered by the claimed invention, a dispersion of the at least one magnetic particle is added to the mixture.

[0060] In a preferred embodiment not covered by the claimed invention, the at least one magnetic particle is dispersed in a suitable dispersion medium. Suitable dispersion media are all dispersion media in which the at least one magnetic particle is not completely soluble. Suitable dispersion media are for example selected from the group consisting of water, water-soluble organic compounds, for example alcohols having from 1 to 4 carbon atoms, particularly preferably water.

[0061] 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 up to 100% by weight, preferably up to 60% by weight, for example 0.5 to 60% by weight, preferably 0.5 to 20% by weight, particularly preferably 0.5 to 10% by weight.

[0062] In one embodiment of the present invention, a high amount of mixture to be treated in the slurry or dispersion is preferred. Therefore, the present invention preferably relates to the process according to the present invention, wherein the amount of mixture to be treated based on the total slurry or dispersion is up to 60% by weight, for example 20 to 60% by weight.

[0063] 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, for example a stirring tank, and stirred by means of devices known to those skilled in the art, for example in a stirring tank by means of a magnetically operated propeller stirrer, for example at a temperature of from 1 to 80°C, preferably at room temperature.

[0064] According to the second embodiment of step (A) of the process according to the present invention, the contacting of the mixture with at least one magnetic particle and at least one surface-modifying substance at the same time is generally carried out by combining the components by methods known to those skilled in the art. For example, this second embodiment of step (A) can be carried out in bulk or in dispersion, preferably in suspension. Suitable dispersion media are for example selected from the group consisting of water, water-soluble organic compounds, for example alcohols having from 1 to 4 carbon atoms, and mixtures thereof. In a particularly preferred embodiment, the dispersion medium is water. In a preferred second embodiment, a dispersion of the at least one magnetic particle and at least one surface-modifying substance is added to the mixture.

[0065] The present invention therefore preferably relates to the process according to the present invention, wherein contacting of the mixture comprising at least one first material and at least one second material with at least one magnetic particle or with at least one magnetic particle and at least one surface-modifying substance at the same time in step (A) is achieved by addition of a mixture, preferably a dispersion, of least one magnetic particle and at least one surface-modifying substance.

[0066] In a further embodiment of the process of the invention, both embodiments of step (A) can be carried out in bulk, i.e. in the absence of a dispersion medium.

[0067] For example, the mixture to be treated and the at least one magnetic particle or at least one magnetic particle and the at least one surface-modifying substance are combined and mixed in the appropriate amounts without a further dispersion medium. Suitable mixing apparatuses are known to those skilled in the art, for example mills such as ball mills.

[0068] Step (A) is generally carried out at a temperature of from 1 to 80 °C, preferably from 10 to 30 °C.

[0069] According to the second embodiment of step (A), wherein at least one magnetic particle and at least one surface-modifying substance are added at the same time, the at least one magnetic particle becomes attached to the at least one first material that is more hydrophobic than the at least one second material by nature and that is further hydrophobized at its surface by the at least one surface-modifying substance. The bond between the two components is based on hydrophobic interactions. There is generally no bonding interaction between the at least one magnetic particle and the hydrophilic component of the mixture, so that these components do not become attached to one another. Thus, addition products of the at least one first, hydrophobic material and the at least one magnetic particle are present alongside the at least one second, hydrophilic material in the mixture after the second embodiment of step (A) of the process according to the present invention.

Step (B):

[0070] The optional step (B) of the process of the invention comprises addition of at least one dispersion medium to the mixture obtained in step (A) to give a dispersion having a suitable concentration.

[0071] In one embodiment, if step (A) is carried out in bulk, the mixture obtained in step (A) comprises at least one first material and at least second material, at least one magnetic particle and optionally at least one surface-modifying substance. If step (A) is carried out in bulk, step (B) 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 (A) in order to obtain a dispersion.

[0072] In the embodiment in which step (A) of the process of the invention is carried out in dispersion, step (B) is preferably not carried out. However, in this embodiment, too, it is possible to carry out step (B), i.e. to add further dispersion medium in order to obtain a dispersion having a lower concentration.

[0073] Suitable dispersion media are all dispersion media which have been mentioned above in respect of step (A). In a particularly preferred embodiment, the dispersion medium in step (B) is water.

[0074] Thus, step (B) comprises either converting the mixture present in bulk from step (A) into a dispersion or converting the mixture which is already in dispersion from step (A) into a dispersion of lower concentration by addition of dispersion media.

[0075] 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 is obtained which is readily stirrable and/or conveyable. In a preferred embodiment, the amount of mixture to be treated based on the total slurry or dispersion is up to 100% by weight, preferably up to 60% by weight, for example 0.5 to 60% by weight, preferably 0.5 to 20% by weight, particularly preferably 0.5 to 10% by weight.

[0076] In one embodiment of the present invention, a high amount of mixture to be treated in the slurry or dispersion is preferred. Therefore, the present invention preferably relates to the process according to the present invention, wherein the amount of mixture to be treated based on the total slurry or dispersion is up to 60% by weight, for example 20 to 60% by weight.

[0077] In a preferred embodiment of the process of the invention, step (B) is not carried out but instead step (A) is

carried out in aqueous dispersion so that a mixture in aqueous dispersion having the correct concentration for use in step (C) of the process of the invention is obtained directly in step (A).

[00778] The addition of dispersion medium in step (B) 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 (C):

[0079] Step (C) of the process not covered by the claimed the invention comprises contacting of the mixture from step (A) or (B) with at least one surface active substance, if this has not been done in step (A), so that the at least one first material, the at least one surface-modifying substance and the at least one magnetic particle become attached to one another.

[0080] Step (C) of the process not covered by the claimed invention is conducted, if at least one surface-modifying active substance is not added in step (A) of the process according to the present invention. According to this first embodiment of the process not covered by the claimed invention, a mixture comprising the at least one first material, the at least one second material, the at least one magnetic particle and optionally at least one dispersion medium, that is obtained in step (A) or (B), is introduced in step (C).

[0081] The at least one surface-modifying substance that is added in step (C) of the process not covered by the claimed invention and preferred embodiments thereof can be selected from the group of compounds of general formula (I) as mentioned in respect of step (A) of the process according to the present invention.

[0082] According to step (C) of the process not covered by the claimed invention, the at least one surface-modifying substance is generally used in an amount which is sufficient to achieve the desired effect. In a preferred embodiment, the at least one surface-modifying substance is added in step (C) of the process according to the present invention in an amount of from 0.001 to 1% by weight, preferably 0.001 to 0.1% by weight in each case based on the total mixture to be treated.

[0083] Step (C) of the process not covered by the claimed invention can in general be conducted according to all methods that are known to the skilled artisan. In particular, the addition according to step (C) of the process according to the present invention can be conducted as mentioned in respect of step (A) of this process.

Step (D):

[0084] Step (D) of the process comprises separation of the addition product from step (A), (B) or (C) from the mixture by application of a magnetic field.

[0085] The "addition product" in the sense of step (D) is the agglomerate that is obtained in step (A) or (C) containing at least one first material, at least one surface active substance and at least one magnetic particle.

[0086] 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.

[0087] Step (D) can be carried out by introducing a permanent magnet into the reactor in which the mixture from step (A), (B) or (C) is present. In a preferred embodiment, a dividing wall composed of nonmagnetic material, for example the wall of the reactor, is present between permanent magnet and mixture to be treated. In a further preferred embodiment of the process of the invention, an electromagnet which is only magnetic when an electric current flows is used in step (D). Suitable apparatuses are known to those skilled in the art.

[0088] In a preferred embodiment, the magnetic separation equipment allows to wash the magnetic concentrate while the separation with a dispersant, preferably water. This washing preferably allows removing inert material from the magnetic concentrate leading to higher grades of the valuables.

[0089] In a preferred embodiment, step (D) is conducted continuously or semi-continuously, wherein preferably the mixture to be treated flows through a 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.

[0090] 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 6 to 13, preferably 8 to 12. In a preferred embodiment, no adjustment of pH-value of the dispersion obtained in step (A) or (B) is necessary.

[0091] 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.

[0092] In a continuous or semi-continuous process the mixture is preferably mixed by turbulent flow, and is preferably not additionally stirred.

[0093] 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.

[0094] 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.

[0095] After step (D) of the process, the agglomerate of at least one first material that is to be separated according to the present invention, at least one surface-modifying substance and at least one magnetic particle is separated from the at least one second material. Preferably both fractions that are obtained are present as dispersions in at least one dispersion medium, preferably in water.

Step (E):

[0096] Optional step (E) of the process of the invention comprises cleavage of the addition product which has been separated off in step (D) to obtain the at least one first material and the at least one magnetic particle separately.

[0097] In a preferred embodiment of the process of the invention, the cleavage in step (E) is carried out in a nondestructive manner, i.e. the individual components present in the dispersion are not changed chemically. For example, the cleavage according to the invention is preferably not affected by oxidation of the hydrophobizing agent, for example to give the oxidation products or degradation products of the hydrophobizing agent. Cleavage can 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 magnetic particle can be recovered in reusable form. In a preferred embodiment, the magnetic particle which has been cleaved off is reused in step (A) of the process according to the present invention.

[0098] In a preferred embodiment, the cleavage in step (E) of the process of the 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.

[0099] Examples of basic compounds which can be used according to the invention are aqueous solutions of basic compounds, for example aqueous solutions of alkali metal and/or alkaline earth metal hydroxides, for example KOH, NaOH, lime water, aqueous ammonia solutions, aqueous solutions of organic amines of the general formula R^2_3N , where the radicals R^2 are selected independently from the group consisting of C_1 - C_8 -alkyl which may optionally be substituted by further functional groups.

[0100] Examples of surface-active compounds which can be used according to the invention are nonionic, anionic, cationic and/or zwitterionic surfactants. In a preferred embodiment, the cleavage is made by the use of biodegradable, preferably nonionic, surfactants with concentrations in the range of the critical micelle concentrations. In a preferred embodiment, the addition product of hydrophobic material and magnetic particle is cleaved by means of biodegradable nonionic surfactants, further preferably added in an amount slightly, for example up to 5%, more preferably up to 3%, above the critical micelle concentration of the surfactant.

[0101] After optional cleavage according to step (E), the at least one first material and the at least one magnetic particle are, according to the invention, present as dispersion in the abovementioned cleavage reagent, preferably in a mixture of water and surfactant. For example, the at least one magnetic particle is separated from the dispersion comprising this at least one magnetic particle and the at least one first material by means of a permanent magnet or electromagnet. Details of the separation are analogous to step (D) of the process of the invention.

[0102] The first material to be separated off, preferably the metal compound to be separated off, is preferably separated from the dispersion medium by drying.

[0103] The process according to the present invention comprises steps (A) second embodiment, (B) and (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 without optional step (E) according to the present invention to obtain the at least one metal in pure form.

[0104] In a further process not covered by the claimed invention, wherein after step (D) or step (E) the following step (F) is conducted:

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

[0105] The magnetic particles or agglomerates obtained in step (D) preferably comprise iron comprising magnetic substances or magnetic particles in addition to at least one first material, being for example at least one precious metal. Because iron is essentially necessary for melting and/or smelting processes to obtain the at least one first material in pure or enriched 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.

[0106] In the case that noble metals are used as first material in combination with iron comprising magnetic particles, no need for further addition of other iron containing compounds may exist. 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.

[0107] In a further embodiment of the process not covered by the claimed invention, step (F) is conducted according to the present invention after step (E).

[0108] Smelting, extracting and/or wet chemical refining are conducted according to methods that are known to the skilled artisan.

Figures:

[0109] Figure 1 shows a diagram, wherein a process for separating valuables from the gangue of an ore according to the prior art, wherein surface-modifying substance and magnetite are added in two steps (diamonds, 1) is compared to the process according to the present invention, wherein surface-modifying substance and magnetite are added in one step (square, 2). The x-axis (4) shows time in minutes, the y-axis (3) shows a value that is corresponding to the particle size in μm .

[0110] In the case of the process according to the present invention, both, surface-modifying substance and magnetite are added at $t = 0$ min (5). In the case of the process according to the prior art, surface-modifying substance is added at $t = 0$ min, and magnetite is added at $t =$ about 37 min (6). (left vertical line). At about 72 min (7) (right vertical line), a surfactant is added to separate the agglomerates, in both cases.

Examples

[0111] A roughly premilled porphyric copper ore from south America (0.66 wt% Cu, 0.029 wt% Mo) is milled to $d_{80} =$ about 40 μm without the addition of any additive. After milling, the pulp having a solid content of 60 wt% is treated with octyl xanthate (400 g/t) and hydrophobic magnetite (3 wt%) in varying orders. Treatment is conducted in a beaker under stirring using an inertly coated paddle mixer. Subsequently, the pulp is diluted to a solid content of 15 wt% and is separated magnetically. Results in respect of recovery and grade of copper and molybdenum are shown in table 1.

Table 1

Examples No.	1	2	3	4	5	6
Time of addition of xanthate [min]	15	15*	30	15	10	5
Time of addition of magnetite [min]	15	15*				
Cu Recovery [wt%]	93	92	89	95	95	95
Mo Recovery [wt%]	94	90	88	94	94	91
Cu Grade [%]	18.2	17.8	17.9	17.9	16.9	17.1
Mo Grade [%]	0.62	0.56	0.61	0.61	0.55	0.53
*reversed order						

[0112] In examples 1 and 2 at $t = 0$ min, the first substance (xanthate or magnetite) is added, after 15 min the other substance (xanthate or magnetite) is added, then it is stirred for 15 min, before agglomerates are treated as mentioned above.

[0113] In examples 3 to 6 both substances (xanthate and magnetite) are added at $t = 0$ min, after stirring for the time as mentioned in table 1, the agglomerates are treated as mentioned above.

[0114] The present invention and the scope thereof is defined by the appended claims. The more generic description of the invention is provided for illustrative purposes only. Embodiments not falling under these claims are for reference purposes only.

Claims

1. 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, which comprises the following steps:

(A) contacting of the mixture comprising at least one first material and at least one second material with at least one magnetic particle and at least one surface-modifying substance at the same time, so that the at least one first material, the at least one surface-modifying substance and the at least one magnetic particle become attached to one another, if appropriate in the presence of at least one dispersant,

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

(C) separation of the addition product from step (A) or (B) from the mixture by application of a magnetic field, (D) if appropriate, cleavage of the addition product which has been separated off in step (C) to obtain the at least one first material and the at least one magnetic particle separately,

wherein the surface-modifying substance modifies the surface of the at least one first material in a way that the at least one first material, the at least one surface-modifying substance and the at least one magnetic particle become attached to one another,

wherein the first material is a hydrophobic metal compound or coal and the second material is a hydrophilic metal compound,

wherein the at least one hydrophobic metal compound is selected from the group consisting of sulfidic ores, oxidic ores, carbonate-comprising ores, noble metals in elemental form, compounds comprising noble metals and mixtures thereof, and

wherein the at least one hydrophilic metal compound is selected from the group consisting of oxidic metal compounds, hydroxidic metal compounds and mixtures thereof.

2. The process according to claim 1, wherein the surface-modifying substance is a substance of the general formula (I)



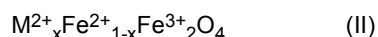
where

A is selected from among linear or branched C₂-C₃₀-alkyl, C₃-C₃₀-heteroalkyl, optionally substituted C₆-C₃₀-aryl, optionally substituted C₆-C₃₀-heteroalkyl, C₆-C₃₀-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.

3. The process according to claim 2, wherein Z is selected from the group consisting of anionic groups -(X)_n-PO₃²⁻, -(X)_n-PO₂S²⁻, -(X)_n-POS₂²⁻, -(X)_n-PS₃²⁻, -(X)_n-PS₂⁻, -(X)_n-POS⁻, -(X)_n-PO₂⁻, -(X)_n-PO₃²⁻, -(X)_n-CO₂⁻, -(X)_n-CS₂⁻, -(X)_n-COS⁻, -(X)_n-C(S)NHOH, -(X)_n-S⁻ where X is selected from the group consisting of O, S, NH, CH₂ and n = 0, 1 or 2, with, if appropriate, cations selected from the group consisting of hydrogen, NR₄⁺ with R being independently of one another hydrogen and/or C₁-C₈-alkyl, hydroxy-substituted C₁-C₈-alkyl or -heteroalkyl, alkali- or earth alkali metals.

4. The process according to any of claims 1 to 3, wherein the at least one magnetic particle is selected from the group consisting of magnetic metals, for example iron, cobalt, nickel and mixtures thereof, ferromagnetic alloys of magnetic metals, for example NdFeB, SmCo and mixtures thereof, magnetic iron oxides, for example magnetite, magnetic hematite, cubic ferrites of the general formula (II)



where

M is selected from among Co, Ni, Mn, Zn and mixtures thereof and

x is ≤ 1,

hexagonal ferrites and mixtures thereof.

5. The process according to any of claims 1 to 4, wherein the dispersion medium is water.

6. The process according to any of claims 1 to 5, wherein the mixture comprising at least one first material and at least one second material is milled to particles having a size of from 100 nm to 100 μm before or during step (A).

7. The process according to any of claims 1 to 6, wherein contacting the mixture comprising at least one first material and at least one second material with at least one magnetic particle and at least one surface-modifying substance at the same time in step (A) is achieved by addition of a mixture, preferably a dispersion, of least one magnetic particle and at least one surface-modifying substance.

Patentansprüche

1. Verfahren zum Abtrennen wenigstens eines ersten Materials aus einem Gemisch, das dieses wenigstens eine erste Material und wenigstens ein zweites Material umfasst, umfassend die folgenden Schritte:

(A) Inkontaktbringen des Gemischs, das wenigstens ein erstes Material und wenigstens ein zweites Material umfasst, mit wenigstens einem magnetischen Partikel und wenigstens einem oberflächenmodifizierenden Stoff gleichzeitig, so dass das wenigstens eine erste Material, der wenigstens eine oberflächenmodifizierende Stoff und das wenigstens eine magnetische Partikel aneinander gebunden werden, gegebenenfalls in Gegenwart wenigstens eines Dispergiermittels,
 (B) gegebenenfalls Zugabe wenigstens eines Dispersionsmediums zu dem bei Schritt (A) erhaltenen Gemisch, um eine Dispersion mit einer geeigneten Konzentration zu ergeben,
 (C) Abtrennen des Additionsprodukts von Schritt (A) oder (B) von dem Gemisch durch Anwendung eines Magnetfelds,
 (D) gegebenenfalls Spalten des Additionsprodukts, das bei Schritt (C) abgetrennt worden ist, um wenigstens ein erstes Material und das wenigstens eine magnetische Partikel getrennt zu erhalten,

wobei der oberflächenmodifizierende Stoff die Oberfläche des wenigstens einen ersten Materials so modifiziert, dass das wenigstens eine erste Material, der wenigstens eine oberflächenmodifizierende Stoff und das wenigstens eine magnetische Partikel aneinander gebunden werden,

wobei das erste Material eine hydrophobe Metallverbindung oder Kohle ist und das zweite Material eine hydrophile Metallverbindung ist,

wobei die wenigstens eine hydrophobe Metallverbindung ausgewählt ist aus der Gruppe bestehend aus sulfidischen Erzen, oxidischen Erzen, carbonathaltigen Erzen, Edelmetallen in elementarer Form, Verbindungen, die Edelmetalle umfassen, und Gemischen davon, und

wobei die wenigstens eine hydrophile Metallverbindung ausgewählt ist aus der Gruppe bestehend aus oxidischen Metallverbindungen, hydroxidischen Metallverbindungen und Gemischen davon.

2. Verfahren gemäß Anspruch 1, wobei der oberflächenmodifizierende Stoff ein Stoff der allgemeinen Formel (I) ist,

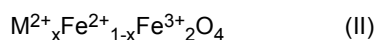


wobei

A ausgewählt ist aus linearem oder verzweigtem C₂-C₃₀-Alkyl, C₃-C₃₀-Heteroalkyl, gegebenenfalls substituiertem C₆-C₃₀-Aryl, gegebenenfalls substituiertem C₆-C₃₀-Heteroalkyl, C₆-C₃₀-Aralkyl, und
 Z eine Gruppe ist, mit deren Hilfe die Verbindung der allgemeinen Formel (I) an das wenigstens eine hydrophobe Material bindet.

3. Verfahren gemäß Anspruch 2, wobei Z ausgewählt ist aus der Gruppe bestehend aus anionischen Gruppen $-(X)_n-PO_3^{2-}$, $-(X)_n-PO_2S^{2-}$, $-(X)_n-POS_2^{2-}$, $-(X)_n-PS_3^{2-}$, $-(X)_n-PS_2^{-}$, $-(X)_n-POS^{-}$, $-(X)_n-PO_2^{-}$, $-(X)_n-PO_3^{2-}$, $-(X)_n-CO_2^{-}$, $-(X)_n-CS_2^{-}$, $-(X)_n-COS^{-}$, $-(X)_n-C(S)NHOH$, $-(X)_n-S^{-}$, wobei X ausgewählt ist aus der Gruppe bestehend aus O, S, NH, CH₂, und n = 0, 1 oder 2, gegebenenfalls mit Kationen ausgewählt aus der Gruppe bestehend aus Wasserstoff, NR₄⁺, wobei R unabhängig voneinander Wasserstoff und/oder C₁-C₈-Alkyl, hydroxysubstituiertes C₁-C₈-Alkyl oder -Heteroalkyl, Alkali- oder Erdalkalimetalle ist.

4. Verfahren gemäß einem der Ansprüche 1 bis 3, wobei das wenigstens eine magnetische Partikel ausgewählt ist aus der Gruppe bestehend aus magnetischen Metallen, beispielsweise Eisen, Cobalt, Nickel und Gemischen davon, ferromagnetischen Legierungen von magnetischen Metallen, beispielsweise NdFeB, SmCo und Gemische davon, magnetischen Eisenoxiden, beispielsweise Magnetit, magnetischem Hämatit, kubischen Ferriten der allgemeinen Formel (II),



wobei

M ausgewählt ist aus Co, Ni, Mn, Zn und Gemischen davon und

$x \leq 1$ ist,

hexagonalen Ferriten und Gemischen davon.

- 5 5. Verfahren gemäß einem der Ansprüche 1 bis 4, wobei das Dispersionsmedium Wasser ist.
6. Verfahren gemäß einem der Ansprüche 1 bis 5, wobei das Gemisch, das wenigstens ein erstes Material und wenigstens ein zweites Material umfasst, vor oder während Schritt (A) zu Partikeln mit einer Größe von 100 nm bis 100 μm gemahlen wird.
- 10 7. Verfahren gemäß einem der Ansprüche 1 bis 6, wobei Inkontaktbringen des Gemischs, das wenigstens ein erstes Material und wenigstens ein zweites Material umfasst, mit wenigstens einem magnetischen Partikel und wenigstens einem oberflächenmodifizierenden Stoff gleichzeitig bei Schritt (A) durch Zugabe eines Gemischs, vorzugsweise einer Dispersion, wenigstens eines magnetischen Partikels und wenigstens eines oberflächenmodifizierenden Stoffs durchgeführt wird.

Revendications

- 20 1. Procédé pour la séparation d'au moins un premier matériau à partir d'un mélange comprenant cet au moins un premier matériau et au moins un deuxième matériau, qui comprend les étapes suivantes :

(A) mise en contact du mélange comprenant au moins un premier matériau et au moins un deuxième matériau avec au moins une particule magnétique et au moins une substance de modification de surface en même temps, de sorte que l'au moins un premier matériau, l'au moins une substance de modification de surface et l'au moins une particule magnétique deviennent fixées les unes avec les autres, le cas échéant en la présence d'au moins un dispersant,

(B) le cas échéant, addition d'au moins un milieu de dispersion au mélange obtenu dans l'étape (A) pour donner une dispersion possédant une concentration appropriée,

(C) séparation du produit d'addition de l'étape (A) ou (B) à partir du mélange par application d'un champ magnétique,

(D) le cas échéant, clivage du produit d'addition qui a été séparé dans l'étape (C) pour obtenir l'au moins un premier matériau et l'au moins une particule magnétique séparément,

la substance de modification de surface modifiant la surface de l'au moins un premier matériau de manière à ce que l'au moins un premier matériau, l'au moins une substance de modification de surface et l'au moins une particule magnétique deviennent fixées les unes avec les autres,

le premier matériau étant un composé métallique hydrophobe ou un charbon et le deuxième matériau étant un composé métallique hydrophile,

l'au moins un composé métallique hydrophobe étant choisi dans le groupe constitué par des minerais sulfurés, des minerais oxydiques, des minerais comprenant un carbonate, des métaux nobles sous forme élémentaire, des composés comprenant des métaux nobles et des mélanges correspondants, et l'au moins un composé métallique hydrophile étant choisi dans le groupe constitué par des composés métalliques oxydiques, des composés métalliques hydroxydiques et des mélanges correspondants.

2. Procédé selon la revendication 1, la substance de modification de surface étant une substance de la formule générale (I)

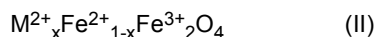


où

A est choisi parmi $\text{C}_2\text{-C}_{30}$ -alkyle linéaire ou ramifié, $\text{C}_3\text{-C}_{30}$ -hétéroalkyle, $\text{C}_6\text{-C}_{30}$ -aryle éventuellement substitué, $\text{C}_6\text{-C}_{30}$ -hétéroalkyle éventuellement substitué, $\text{C}_6\text{-C}_{30}$ -aralkyle, et
Z est un groupe au moyen duquel le composé de la formule générale (I) se lie à l'au moins un matériau hydrophobe.

3. Procédé selon la revendication 2, Z étant choisi dans le groupe constitué par des groupes anioniques $-(X)_n-PO_3^{2-}$, $-(X)_n-PO_2S^{2-}$, $-(X)_n-POS_2^{2-}$, $-(X)_n-PS_3^{2-}$, $-(X)_n-PS_2^-$, $-(X)_n-POS^-$, $-(X)_n-PO_2^-$, $-(X)_n-PO_3^{2-}$, $-(X)_n-CO_2^-$, $-(X)_n-CS_2^-$, $-(X)_n-COS^-$, $-(X)_n-C(S)NHOH$, $-(X)_n-S^-$, où X est choisi dans le groupe constitué par O, S, NH, CH₂ et n = 0, 1 ou 2, avec, le cas échéant, des cations choisis dans le groupe constitué par hydrogène, NR₄⁺ avec R étant indépendamment les uns des autres hydrogène et/ou C₁-C₈-alkyle, C₁-C₈-alkyle substitué par hydroxy ou C₁-C₈-hétéroalkyle substitué par hydroxy, des métaux alcalins ou alcalino-terreux.

4. Procédé selon l'une quelconque des revendications 1 à 3, l'au moins une particule magnétique étant choisie dans le groupe constitué par des métaux magnétiques, par exemple le fer, le cobalt, le nickel et des mélanges correspondants, des alliages ferromagnétiques de métaux magnétiques, par exemple NdFeB, SmCo et des mélanges correspondants, des oxydes de fer magnétiques, par exemple la magnétite, l'hématite magnétique, des ferrites cubiques de la formule générale (II)



où

M est choisi parmi Co, Ni, Mn, Zn et des mélanges correspondants et

x est ≤ 1,

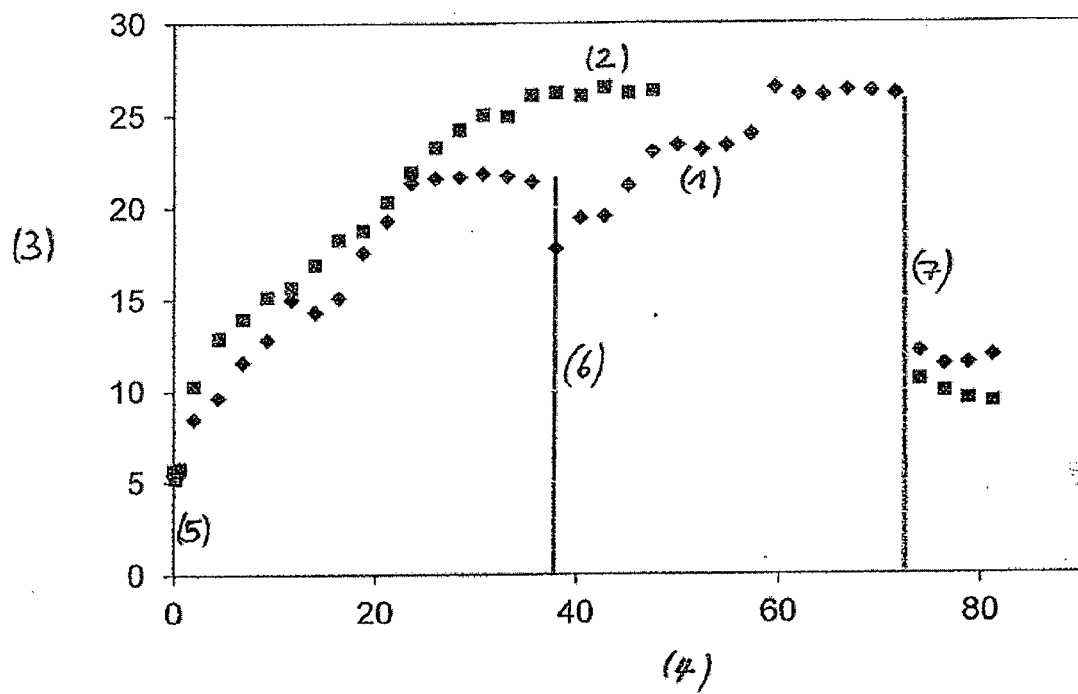
des ferrites hexagonales et des mélanges correspondants.

5. Procédé selon l'une quelconque des revendications 1 à 4, le milieu de dispersion étant l'eau.

6. Procédé selon l'une quelconque des revendications 1 à 5, le mélange comprenant au moins un premier matériau et au moins un deuxième matériau étant broyé en particules possédant une taille allant de 100 nm à 100 μm avant ou pendant l'étape (A).

7. Procédé selon l'une quelconque des revendications 1 à 6, la mise en contact du mélange comprenant au moins un premier matériau et au moins un deuxième matériau avec au moins une particule magnétique et au moins une substance de modification de surface en même temps dans l'étape (A) étant réalisée par ajout d'un mélange, préférablement d'une dispersion, d'au moins une particule magnétique et d'au moins une substance de modification de surface.

Fig. 1



REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- WO 020066168 A1 [0004]
- US 4657666 A [0005]
- US 4834898 A [0006]
- WO 2007008322 A1 [0008]
- US 2011240527 A1 [0009]
- WO 2011058039 A1 [0009]
- WO 2009030669 A1 [0009]
- US 5051199 A [0026]
- EP 1200408 B1 [0054]

Non-patent literature cited in the description

- **S. R. GRAY ; D. LANDBERG ; N. B. GRAY.** *Extrac-tive Metallurgy Conference, Perth, 02 October 1991, 223-226* [0007]