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(54) Title: AMINE FORMULATIONS FOR REVERSE FROTH FLOTATION OF SILICATES FROM IRON ORE

(57) Abstract: The present invention relates to a reverse froth flotation process for removal of silicates from iron ore having $K_80 \geq 110 \mu\text{m}$ using formulations comprising alkyl ether diamine and alkyl ether monoamine, alkylamine or alkyl diamine. The collecting composition comprises a first component a) which can be described by the general formula (I) $\text{R}^1\text{O-A-NH}(\text{CH}_2)_n\text{NH}_2$, wherein R^1 is a straight or branched hydrocarbyl group with 12-15 carbon atoms, A is a group $\text{CH}_2\text{CHXCH}_2$ -, wherein X is hydrogen or a hydroxyl group, and n is a number 2-6; and a second component b) which is suitably selected from the group of compounds described by the formulae R^2NH_2 (Ha), $\text{R}^3\text{NHC}_3\text{H}_6\text{NH}_2$ (UIa), $\text{R}^2\text{QC}_3\text{H}_3\text{NH}_2$ (lib), and $\text{R}^3\text{OC}_3\text{H}_6\text{NHC}_3\text{H}_6\text{NH}_2$ (UIb), wherein R^2 is a straight or branched hydrocarbyl group with 12-24 carbon atoms and R^3 is a straight or branched hydrocarbyl group with 16-24 carbon atoms.



WO 2008/077849 A1

AMINE FORMULATIONS FOR REVERSE FROTH FLOTATION OF SILICATES FROM IRON ORE

The present invention relates to a reverse froth flotation process for removal of
5 silicates from iron ore having $K_80 \geq 110 \mu\text{m}$ using formulations comprising alkyl
ether diamine and alkyl ether monoamine, alkylamine or alkyl diamine.

Iron ore often contains considerable amounts of silicates. The presence of
silicates has a detrimental effect on the quality of the iron, and it is therefore
10 essential that the silicate content of the iron mineral can be considerably
reduced. A common process of removing silicates from iron ore is reversed
froth flotation, where the silicates are enriched in the flotite and leave the
system with the froth, and the iron ends up in the bottom fraction.

When using reverse froth flotation, generally the iron ore bottom fraction either
15 contains a low level of SiO_2 and has a low recovery of iron, or it contains a high
level of SiO_2 and has a high recovery of iron. In particular, the presence of
coarse silicates (particle size $\geq 110 \mu\text{m}$) in the system has a negative effect on
the iron recovery. Various solutions have been proposed in the prior art to
increase iron recovery and reduce SiO_2 levels. Very often these solutions have
20 involved grinding the ores to fine particles.

Grinding (also referred to as milling) is thus an important step of the flotation
process, which step is necessary to liberate the valuable species in the ore. The
particle size to which an ore must be size-reduced in order to liberate the
25 mineral values from associated gangue or non-values is called the liberation
size, and this will vary from ore to ore. In theory, the ore should not be ground
further when the liberation size of the ore has been reached, since this will
unnecessarily consume more energy and produce comparatively larger
fractions of the very fine particles which are detrimental to the flotation process.
30 However, as is stated in *Mineral Processing Technology*, sixth edition, by B.A.
Wills, page 278, "...the optimum grinding size of the particles depends not only

on their grain size, but also on their floatability. Initial examination of the ore should be made to determine the degree of liberation in terms of particle size in order to estimate the required fineness of grind. Testwork should then be carried out over a range of grinding sizes in conjunction with flotation tests in order to determine the optimum mesh of grind. In certain cases, it may be necessary to overgrind the ore in order that the particles are small enough to be lifted by the air-bubbles." Accordingly, it is not uncommon to mill ores to particle sizes below the liberation size in order to improve the flotation process, particularly to reduce the SiO₂ level in the iron-fraction. It is clear that from an energy and milling-efficiency point of view, such overmilling is undesired.

It is noted that in order to describe the distribution of particle sizes in an ore, the K_{80} value is generally used. The factor K_{80} is defined as the sieve opening through which 80% by weight of the material of the mineral sample passes. If an ore has a K_{80} value of 110 μm , this means that 80% by weight of the material in the mineral sample will pass through a 110 μm sieve, and thus 20% by weight of the material of the sample will consist of particles having a diameter that is larger than 110 μm .

US 6,076,682 discloses a process for enriching iron mineral from a silicate-containing iron ore by carrying out a reverse froth flotation in the presence of a silicate collecting agent containing a combination of at least one primary ether monoamine and at least one primary ether polyamine, where each of the ether amines contains an aliphatic hydrocarbyl group having 6-22 carbon atoms and the weight ratio of ether monoamine to ether polyamine is 1:4-4:1, and a depressing agent for the iron mineral. The working examples were performed with an iron ore having a K_{80} of about 75 μm .

SE 421 177 discloses a way to enrich oxidic minerals, especially iron minerals, by separation of silicate-containing gangues by foam flotation using a collector that is a combination of C8-C24 alkyl, preferably C10-C16 alkyl, fatty amines

(mono-, di- or polyamines) and C8-C24 alkyl, preferably C8-C14-alkyl, ether diamines. The weight ratio of ether diamine to fatty amine is defined to be larger than 1.1:1. The K_{80} for the iron ore used in the working examples of this patent publication is 85 μm .

- 5 CA-A1 -2 205 886 relates to compositions of matter comprising a blend of (a) an amine component, which is one or more compounds selected from the group consisting of alkyl amines, alkyl diamines, alkyl polyamines, ether amines and ether polyamines and mixtures thereof; and (b) a C3-C24 carboxylic acid or mixtures thereof; for use e.g. in the froth flotation of silica from iron ore. This
10 patent publication is silent about the K_{80} -value of the mineral samples flotated.

In all this art the ores were milled to relatively small particles, most likely to facilitate the flotation process in order to optimize SiO_2 removal. The presence of very small particles also indicates that the ore is milled to below the liberation
15 size. However, there is still a desire to be able to flotata silicate-containing iron ores having a $K_{80} \geq 110 \mu\text{m}$, since there will be less energy consumption if the ores to be flotated do not need to be ground to a smaller size and because it was found that the liberation size is often greater than 110 μm . Furthermore if the ore is less finely ground, there will be lower iron fine particle losses, further
20 increasing the iron yield.

When evaluating iron ores with a $K_{80} \geq 110 \mu\text{m}$ it was observed that the collectors used in the prior art for the more finely ground ores do not work very well, which again explains why traditionally smaller particle sizes were used.
25 Therefore, there still is a need for a process wherein ores with a $K_{80} \geq 110 \mu\text{m}$, comprising an iron-mineral, can be reverse flotated to effectively remove silicate, using collecting agents that at the same time will not have a negative effect on the recovery of iron.

Now it has surprisingly been found that low silicate levels as well as high recovery of iron can be achieved for silicate-containing iron ores having $K_{80} \geq 110 \mu\text{m}$, preferably $\geq 115 \mu\text{m}$ and most preferably $\geq 120 \mu\text{m}$, by reverse flotation of the ore using a specific collecting composition comprising

- 5 a) one or more C₁₂-C₁₅ alkyl ether diamines
 b) one or more C₁₂-C₂₄, preferably C₁₂-C₁₈, and most preferably C₁₃-C₁₈, alkyl ether monoamines, one or more C₁₂-C₂₄, preferably C₁₂-C₁₈, alkyl monoamines, one or more C₁₆-C₂₄, preferably C₁₆-C₁₈, alkyl ether diamines or one or more C₁₆-C₂₄, preferably C₁₆-C₁₈, alkyl diamines, or mixtures
 10 thereof
 c) and optionally a depressing agent for the iron mineral,
 wherein the weight ratio between a) and b) is 1:5 to 5:1, preferably 1:4 to 4:1, more preferably 1:4 to 3:1.

This surprising effect is probably due to the fact that this mixture of flotating aids
 15 is capable of flotating larger silicate particles in these reverse flotation processes.

The maximum K_{80} value from a mineralogical point of view is determined by the milling needed to liberate the minerals. Thus, the less milling needed, the higher
 20 the value of K_{80} . Preferably, the K_{80} of the ore to be processed in accordance with the invention is at most 200 μm , more preferably at most 180 μm , even more preferably at most 160 μm , and most preferably at most 150 μm .

The first component a) is described by the general formula

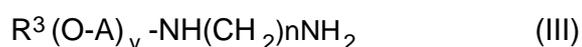


wherein R^1 is a straight or branched hydrocarbyl group with 12-15 carbon atoms, A is a group $-CH_2CHXCH_2-$, wherein X is hydrogen or a hydroxyl group, preferably hydrogen, and n is a number 2-6, preferably 2-3, and most preferably 3;

the second component b) of the formulation is selected from the group of compounds described by the formulae



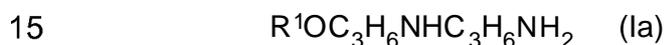
wherein R^2 is a straight or branched hydrocarbyl group with 12-24, preferably 12-18, and most preferably 13-18 carbon atoms, $x = 0$ or 1, preferably 0, and A is as described above; and



wherein R^3 is a straight or branched hydrocarbyl group with 16-24, preferably 16-18 carbon atoms, $y = 0$ or 1, preferably 0, and A and n are as described above;

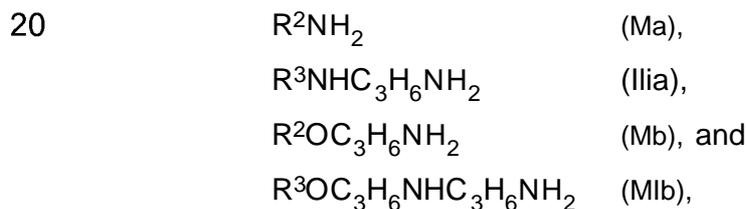
and wherein the weight ratio between a) and b) is 1:5 to 5:1.

In another embodiment, the first component a) of the formulation is of the formula



wherein R^1 is a straight or branched, preferably branched, hydrocarbyl group with 12-15 carbon atoms, and

the second component b) of the formulation is selected from the group of compounds described by the formulae



wherein R^2 is a straight or branched hydrocarbyl group with 12-24, preferably 12-18, and most preferably 13-18 carbon atoms, and R^3 is a straight or branched hydrocarbyl group with 16-24, preferably 16-18 carbon atoms.

Most preferred are the embodiments where component b) has formula Ma or IIa.

For any embodiment the weight ratio between a) and b) is 1:5 to 5:1, preferably 1:4 to 4:1, and most preferably 1:4 to 3:1.

In embodiments where b) is a compound of formula (III) it is especially preferred that the weight ratio between a) and b) is $\leq 1:1$, preferably in the range 1:4 to 1:1, but for the other embodiments the wider range is more applicable.

The use of alkyl monoamines according to formula (Ma) as component b) could be advantageous for economic reasons, since alkyl monoamines generally are cheaper than alkyl diamines and alkyl ether mono- and diamines. The compositions containing (Ma) also are easy to formulate, and the collecting compositions are very effective.

Compositions where component b) is an alkyl diamine according to formula (IIia) are also effective, but in this case compounds having saturated alkyl chains have a greater risk of precipitating, and thus compounds having unsaturated alkyl chains are more suitable.

Compositions where b) is an alkyl ether monoamine according to formula (Mb) or an alkyl ether diamine of formula (MIb) can suitably be used at low temperatures, compounds having branched alkyl chains in particular will confer desirable physical properties on the compounds, such as lower pour points.

Suitable examples of groups R^1 are dodecyl, 2-butyloctyl, methyl-branched C13-alkyl (isothdecyl), tetradecyl, and methyl-branched C15-alkyl. Compounds having a branched alkyl group are especially preferred.

Suitable examples of groups R^2 are dodecyl, 2-butyloctyl, methyl-branched C13-alkyl (isotridecyl), tetradecyl, C14-C15-alkyl, methyl-branched C15-alkyl, hexadecyl, C16-C17-alkyl, octadecyl, tallow alkyl, rapeseed alkyl, soya alkyl, oleyl, and erucyl.

Suitable examples of groups R^3 are hexadecyl, octadecyl, C16-C17-alkyl, tallow alkyl, rapeseed alkyl, soya alkyl, oleyl, linoleyl, linolenyl, erucyl, and behenyl. Compounds having branched alkyl groups are especially preferred, and among

the compounds derived from natural sources those having unsaturated alkyl chains are especially preferred, because they are easier to formulate.

5 Examples of suitable alkyl ether diamines to be used in the collecting compositions as component a) are N-[3-(dodecoxy)propyl]-1,3-propane diamine, N-[3-(2-butyloctoxy)propyl]-1,3-propane diamine, N-[3-(tridecoxy)propyl]-1,3-propane diamine, N-[3-(tetradecoxy)propyl]-1,3-propane diamine, and N-[3-(C15-alkoxy)propyl]-1,3-propane diamine.

10 Examples of suitable alkyl ether amines to be used in the formulations are 3-(dodecoxy)propylamine, 3-[(coco alkyl)oxy]propylamine, 3-(2-butyloctoxy)propylamine, 3-(isothdecoxy)propylamine, 3-(tetradecoxy)propylamine, 3-(C14-C15-alkoxy)propylamine, 3-(hexadecoxy)propylamine, 3-(octadecoxy)propylamine, 3-[(rapeseed alkyl)oxy]propylamine, 3-[(soya alkyl)oxy]propylamine, 3-(octadecenoxy)propylamine, 3-[(tallow alkyl)oxy]propylamine, and 3-(erucoxy)-
15 propylamine.

Examples of suitable alkyl monoamines to be used in the formulations are n-dodecyl amine, (coco alkyl)amine, n-tetradecyl amine, n-hexadecyl amine, n-octadecyl amine, oleyl amine, (tallow alkyl)amine, (rapeseed alkyl)amine, (soya alkyl)amine, and erucyl amine.

20 Examples of suitable alkyl diamines to be used in the formulations are N-hexadecyl-thmethylene diamine, N-octadecyl-thmethylene diamine, N-oleyl-trimethylene diamine, N-(rapeseed alkyl)-thmethylene diamine, N-(soya alkyl)-trimethylene diamine, N-(tallow alkyl)-thmethylene diamine, N-linoleyl-trimethylene diamine, N-linolenyl-thmethylene diamine, N-erucyl-trimethylene
25 diamine, and N-behenyl-thmethylene diamine.

Unprotonated amines with the formulae described above (formulae I-V) are difficult to disperse in mineral/water systems without the aid of heating or vigorous stirring. Even with heating and stirring, the dispersions are not stable.

30 A common practice for improving the dispersibility of amines is to prepare the

corresponding ammonium salts by adding acid to the amine, forming at least 20% by mole ammonium salt, preferably before the amine compounds are diluted with water. Examples of suitable acids are lower organic acids, such as formic acid, acetic acid, and propionic acid; and inorganic acids, such as hydrochloric acid. Complete formation of ammonium salt is not needed to form a stable dispersion. In an aqueous mixture the amine compounds are therefore suitably present partly as ammonium salts. For example, 20-70, preferably 25-50% of the amine groups are transferred to ammonium groups, which may be achieved by adding c. 10% by weight acetic acid to the amine compounds of the invention.

Preferably, the flotation is performed in the conventional pH-range of 8-11 in order to obtain the right surface charge of the minerals.

A conventional depressing agent, such as a hydrophilic polysaccharide, e.g. different kinds of starches, may be used in a conventional quantity sufficient to cover the iron ore surface in the amount needed. The depressing agent is normally added in an amount of 10 to 1,000 g per tonne of ore.

An additional way of improving the efficiency of the system according to the invention is to add a froth regulator. Although froth regulators such as methylisobutyl carbinol and alcohols having a C6-C12 alkyl chain, such as 2-ethylhexanol, and alcohols alkoxylated with ethylene oxide and/or propylene oxide, e.g. propoxylated methanol and other ethoxylated/propoxylated short-chain alcohols, are conventionally used, the addition of a froth regulator to the flotation systems comprising our claimed collectors will surprisingly result in a better iron recovery. This is in contrast with prior art flotation compositions containing compounds having shorter chain lengths. For such systems we found that frothers typically have an adverse effect.

Further conventional additives may be added to the flotation system, such as pH-regulating agents, co-collectors, and extender oils.

The principal ores of iron which are suitable for treatment according to the invention are hematite and magnetite ores.

5

The present invention is further illustrated by the following examples.

EXAMPLES

10 **General Experimental**

Flotation preparation

Collector (a+b) + frother

1 g of collector + frother (0.9 g amino compounds (a+b) neutralized with 10% by weight of acetic acid + 0.1 g frother) was diluted with 99 g of distilled water. The solution was stirred for at least 30 min before use.

15

In all formulations containing frother, 2-ethylhexanol is used as the frother in an amount of 10% by weight. Frother is added to all formulations below unless otherwise stated.

Depressant (c) (optional)

20 1% by weight solution of depressant was used. 4 g of unmodified regular corn starch containing approximately 73% amylopectin and 27% amylase (Sigma Aldrich) were diluted in 56 g of distilled water. 20 g of 5% by weight NaOH solution were added slowly. The solution was stirred until a gel formed and then an additional 320 ml of distilled water were added.

25 Flotation procedure

The ground ore sample (770 g) was (optionally) conditioned with depressant c for 5 min in the flotation cell at a concentration of 60% by weight of solid in water, and then additional water was added until the concentration of solid was 40% by weight (= 40% pulp density). All water added during the flotation was tap water. The speed of the rotor was 1,000 rpm. The pH of the 40% pulp was

30

then adjusted to 10.5 with 5% NaOH solution, after which the components a + b of the collector composition + frother were added as a 1% by weight water solution. The actual dosages are described in each of the examples. The dosages are chosen according to recommendations for the specific ore samples used. The alkaline pulp with the added components was conditioned for 1 min before the air and the automatic froth scrapers were turned on. The flotation was performed at 20-25 °C using an air flow of 3 l/min and a scraping frequency of 15 scrapes/min. The pulp level was kept constant by the addition of water below the pulp surface. The flotation was continued until complete exhaustion of mineralized froth was achieved.

The flotation was performed in a sequence with three additions of collector and optional frother followed by a flotation step after each addition, so called step-wise rougher flotation. Each froth product was dried, weighed, and analyzed with respect to SiO_2 content. After completion of the flotation, the bottom concentrate was withdrawn, dried, and analyzed with respect to SiO_2 content and Fe_2O_3 content. For each completed flotation experiment the mass balance and SiO_2 grades were used to calculate the iron recovery and SiO_2 grade in each flotation step, and these results were then plotted in a grade-recovery graph. From this graph the iron recovery was determined by interpolation at a given SiO_2 grade for this specific flotation experiment. In the Tables below, this SiO_2 grade is set at 2.0%.

Sieve analyses

The sieve analyses of the mineral samples were performed in accordance with BS 1796 and DIN 661 65, with the sieves used conforming to the standard DIN ISO 331 0/1. BS 1796 generally describes a sieve analysis using a shaking machine, the latter being adapted in accordance with DIN 661 65. A detailed description of the sieve analysis, based on BS 1976, is found in B.A. Wills, *Mineral Processing Technology*, 6th Ed, 1997, pages 96-1 00.

Example 1

Iron ore containing 73.3% Fe_2O_3 and 24.8 % by weight of SiO_2 was used in this Example to illustrate the invention.

The sieve analysis for this ore is displayed in Table 1.

5

Table 1

Sieve analysis $K_{80} = 124\mu\text{m}$	
Sieve aperture μm	Accumulated weight quantity of ore %
160	89.1
125	80.7
90	68.6
75	61.5
50	46.4
32	27.6

Example 1a

In this example formulations containing an ether diamine and an ether monoamine are used for flotating the ore exhibiting the sieve analysis of Table 1. All formulations contain 10% by weight of 2-ethylhexanol as a frother. The used dosage levels are 50, 30, and 30 g/t of ore (corresponding to 34.7, 20.8, and 20.8 mg of components a+b and 3.9, 2.3, and 2.3 mg of frother added to the flotation cell, respectively).

15

Table 2

Exp. No.	Reagent	Fe-rec. %	SiO ₂ %
	<i>Experiments relating to mixtures of alkyl ether diamines and alkyl ether monoamines</i>		
29	N-(3-Isotridecoxypropyl)-1,3-propane diamine (Comparison) ¹	91.3	2.0
120	N-(3-Isotridecoxypropyl)-1,3-propane diamine/ N-(C8-C10 alkoxypropyl)amine (50/50) (Comparison) ²	88.9	2.0
52	N-(3-Isotridecoxypropyl)-1,3-propane diamine/ N-(C12 alkoxypropyl)amine (50/50)	94.1	2.0
54	N-(3-Isotridecoxypropyl)-1,3-propane diamine/ N-(C14-C15 alkoxypropyl)amine (50/50)	94.4	2.0

¹see US 3 363 758

²see US 6 076 682

5 Flotations Nos. 120, 52, and 54 show that a better effect is obtained when the ether monoamine component has a hydrophobic group containing 12 or more carbon atoms.

Example 1b

10 In this example formulations containing an ether diamine and an alkyl monoamine or alkyl diamine are used for flotating the ore exhibiting the sieve analysis of Table 1. All formulations contain 10% by weight of 2-ethylhexanol as a frother. The used dosage levels are 50, 30, and 30 g/t of ore (corresponding to 34.7, 20.8, and 20.8 mg of components a+b and 3.85, 2.3, and 2.3 mg of frother added to the flotation cell, respectively).

Table 3

Exp. No.	Reagent	Fe-rec. %	SiO ₂ %
	<i>Experiments relating to mixtures of alkyl ether diamines and alkyl monoamines</i>		
29	N-(3-Isotridecoxypropyl)-1,3-propane diamine (Comparison) ¹	91.3	2.0
87	N-(3-Isotridecoxypropyl)-1,3-propane diamine/ oleyl amine (50/50)	92.3	2.0
114	N-(3-Isotridecoxypropyl)-1,3-propane diamine/ oleyl amine (33.3/66.7)	94.5	2.0
113	Oleyl amine (Comparison)	90.5	2.0
50	N-(3-Isotridecoxypropyl)-1,3-propane diamine/ (Coco alkyl)amine (55.5/45.5)	93.2	2.0
	<i>Experiments relating to mixtures of alkyl ether diamines and alkyl diamines</i>		
29	N-(3-Isotridecoxypropyl)-1,3-propane diamine (Comparison) ¹	91.3	2.0
55	N-(3-Isotridecoxypropyl)-1,3-propane diamine/ N-(tallow alkyl)-1,3-propane diamine (50/50)	93.4	2.0
76	N-(3-Isotridecoxypropyl)-1,3-propane diamine/ N-(tallow alkyl)-1,3-propane diamine (20/80)	94.5	2.0
75	N-(tallow alkyl)-1,3-propane diamine (Comparison)	Too little foam	-
29	N-(3-Isotridecoxypropyl)-1,3-propane diamine (Comparison) ¹	91.3	2.0
121	N-(3-Isotridecoxypropyl)-1,3-propane diamine/ N-(oleyl)-1,3-propane diamine (66.7/33.3)**	92.6	2.0
122	N-(3-Isotridecoxypropyl)-1,3-propane diamine/ N-(oleyl)-1,3-propane diamine (33.3/66.7)**	94.5	2.0
126	N-(oleyl)-1,3-propane diamine (Comparison)**	90.3	2.0
123	N-(C12 alkoxypropyl)-1,3-propane diamine/ N-(coco alkyl)-1,3-propane diamine (66.6/33.4) (Comparison)	89.3	2.0
124	N-(3-Isotridecoxypropyl)-1,3-propane diamine/ N-(coco alkyl)-1,3-propane diamine (66.6/33.4) (Comparison)	89.9	2.0
125	N-(3-Isotridecoxypropyl)-1,3-propane diamine/ N-(coco alkyl)-1,3-propane diamine (33.4/66.6) (Comparison)	88.4	2.0

¹see US 3 363 758

*For the comparison experiment it was not possible to perform the flotation due to the weak foam formation.

** the oleyl group is derived from rapeseed oil

Flotations Nos. 29, 55, 76, and 75 show that a synergistic effect is achieved by using a combination of an alkyl ether diamine and an alkyl diamine in the collecting composition, as compared to using the single compounds.

5 Flotations Nos. 29, 121, 122, and 126 show that the use of collecting compositions containing an alkyl ether diamine and an alkyl diamine where a higher amount of the alkyl diamine is present is beneficial, but that the use of the alkyl diamine alone is detrimental.

10 Flotations Nos. 29, 87, 114, and 113 show that the use of collecting compositions containing an alkyl ether diamine and an alkylamine where a higher amount of the alkylamine is present is beneficial, but that the use of the alkylamine alone is detrimental.

15 Flotations Nos. 123, 124, 125, and 50 show that when using a collecting composition containing an ether diamine and an alkyl diamine where the alkyl diamine has a coco alkyl hydrophobic group (which is about C₁₂C₁₄) or lower, the iron recovery is not very good, whereas for a collecting composition containing an alkyl ether diamine and an alkyl monoamine, a coco alkyl hydrophobic group is sufficient to obtain a good iron recovery.

Example 2

20 A comparison test was performed using an ore sample where the ore having the sieve analysis displayed in Table 1 had been further sieved to remove the coarser particles. The sieve analysis of this sample is displayed in Table 6. The ore sample displayed in Table 6 contains 72.1 % Fe₂O₃ and 26.5% by weight of SiO₂.

25

Table 6

Sieve analysis $K_{80} = 79.5 \mu\text{m}$	
Sieve aperture Mm	Accumulated weight quantity of ore %
160	98.8
125	95.7
90	89.0
75	76.8
50	55.3
32	27.8

In this example formulations containing an alkyl ether diamine and an alkyl monoamine or an alkyl ether diamine and an alkyl ether monoamine are used for flotation of the coarser particle ore (C) exhibiting the sieve analysis of Table 1 ($K_{80} = 124 \mu\text{m}$) as compared to the finer particle ore (F) exhibiting the sieve analysis of Table 6 ($K_{80} = 79.5 \mu\text{m}$). All formulations contain 10% by weight of 2-ethylhexanol as a frother. The used dosage levels are 50, 30, and 30 g/t of ore (corresponding to 34.7, 20.8, and 20.8 mg of components a+b and 3.9, 2.3, and 2.3 mg of frother added to the flotation cell) for the ore sample described in Table 6.

Table 7

Exp. No.	Reagent	Fe-recovery %		SiO ₂ %
		K ₈₀ =79.5μm	K ₈₀ =124μm	
40(F) ³ , 114(C) ⁴	N-(3-Isotridecoxypropyl)-1,3-propane diamine/ oleyl amine (33.3/66.7)	92.9 (Comp.)	94.5	2.0
41(F) ³ , 52(C) ⁴	N-(3-Isotridecoxypropyl)-1,3-propane diamine/ N-(C12 alkoxypropyl)amine (50/50)	92.0 (Comp.)	94.1	2.0
42(F) ³ , 94(C) ⁴	N-(3-Isotridecoxypropyl)-1,3-propane diamine/ N-(Isotridecoxypropyl)amine (50/50)	Too little foam (Comp.)	94.7	2.0*
64(F) ³ , 58(C) ⁴	N-(3-Isotridecoxypropyl)-1,3-propane diamine/ (Coco alkyl)amine (66.6/33.4)	90.4 (Comp.)	93.2	2.0
65(F) ³ , 59(C) ⁴	N-(C8-C10-alkoxypropyl)- 1,3-propane diamine/ (Coco alkyl)amine (66.6/33.4)	86.5 (Comp.)	86.4 (Comp.)	2.0
66(F) ³ , 62(C) ⁴	N-(3-Isotridecoxypropyl)-1,3-propane diamine/ (C10-alkyl)amine (66.6/33.4)	88.5 (Comp.)	88.8 (Comp.)	2.0

* For the comparison experiment it was not possible to perform the flotation due to the weak foam formation.

Experiment performed on the finer particle ore

5 ⁴Experiment performed on the coarser particle ore

In all cases the specific collecting compositions according to the present invention work better for the coarse ore (K₈₀= 124 μm) than for the fine ore (K₈₀ = 79.5). For the collecting compositions outside the scope of the present invention, there is no difference between the flotations performed on fine and coarse ores, and the Fe-recovery is smaller than for the compositions according to the invention.

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Example 3

In this example the effect of adding a frother to the collecting compositions is investigated.

The ore of Table 1 was used. The used dosage levels when 10% frother (2-ethylhexanol) is used are 50, 30, and 30 g/t of ore (corresponding to 34.7, 20.8, and 20.8 mg of components a+b and 3.85, 2.3, and 2.3 mg of frother added to the flotation cell, respectively). The used dosage levels when no frother is added are 50, 30, and 30 g/t (corresponding to 38.6, 23.1, and 23.1 mg of components a+b added to the flotation cell).

10

Table 8

Exp No	Reagent	Fe-rec. %		SiO ₂ %
		Frother	No frother	
123 ⁵ , 80 ⁶	N-(C12 alkoxypropyl)-1,3-propane diamine/ N-(coco alkyl)-1,3-propane diamine (66.6/33.4) (Comparison)	89.3	91.2	2.0
124 ⁵ , 81 ⁶	N-(3-Isotridecoxypropyl)-1,3-propane diamine/ N-(coco alkyl)-1,3-propane diamine (66.6/33.4) (Comparison)	89.9	91.3	2.0
55 ⁵ , 79 ⁶	N-(3-Isotridecoxypropyl)-1,3-propane diamine/ N-(tallow alkyl)-1,3-propanediamine (50/50)	93.4	91.7	2.0

Experiment ⁵ performed in the presence of a frother

⁶Experiment performed without any frother

15 This example shows that for the composition according to the invention, it is advantageous to add a frother, whereas for the comparison compositions containing compounds having shorter chain lengths, it is more advantageous not to add a frother.

CLAIMS

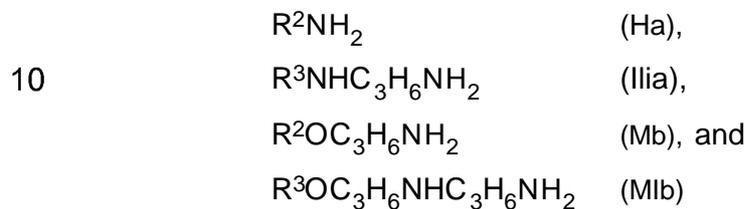
1. A process for enriching an iron mineral from a silicate-containing iron ore containing coarse silicates having $K_8O \geq 110 \mu\text{m}$ by reverse flotation of the ore using a collecting composition comprising
- 5 a) one or more compounds having the formula
- $$R^1O-A-NH(CH_2)_nNH_2 \quad (I)$$
- wherein R^1 is a straight or branched hydrocarbyl group with 12-15 carbon atoms, A is a group $-CH_2CHXCH_2-$, wherein X is hydrogen or a hydroxyl group, preferably hydrogen, and n is a number 2-6, preferably 2-3, and
- 10 most preferably 3; and
- b) a compound selected from the group of compounds described by the formulae
- $$R^2(O-A)_x-NH_2 \quad (II)$$
- 15 wherein R^2 is a straight or branched hydrocarbyl group with 12-24, preferably 12-18, and most preferably 13-18 carbon atoms, $x = 0$ or 1, and A is as described above; and
- $$R^3(O-A)_y-NH(CH_2)_nNH_2 \quad (III)$$
- wherein R^3 is a straight or branched hydrocarbyl group with 16-24, preferably
- 20 16-18 carbon atoms, $y = 0$ or 1, and A and n are as described above; and wherein the weight ratio between a) and b) is 1:5 to 5:1 .
2. A process according to claim 1 wherein b) is III and the weight ratio between a) and b) is 1:4 to 1:1 .
- 25 3. A process according to claim 1-2 comprising a further component c) which is a depressing agent for the iron mineral.
4. A process according to claim 3 wherein the depressing agent is chosen
- 30 from the group of hydrophilic polysaccharides.

5. A process according to claims 1-4 wherein the first component a) of the formulation is described by the formula



5 wherein R^1 is a straight or branched hydrocarbyl group with 12-15 carbon atoms, and

the second component b) of the formulation is selected from the group of compounds described by the formulae



15 wherein R^2 is a straight or branched hydrocarbyl group with 12-24 carbon atoms and R^3 is a straight or branched hydrocarbyl group with 16-24 carbon atoms.

6. A process according to claims 1-5 wherein component b) has formula Ia or IIa.

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7. A process according to claims 1-6 wherein the collecting composition further contains a frother.

8. A process according to claim 7 wherein the frother is 2-ethylhexanol.

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9. A process according to claims 1-8 wherein the amine components in the collecting composition are present as ammonium salts in an amount of at least 20% by mole.

10. A process according to claims 1-9 where the collecting composition comprises a) N-(3-isothdecoxypropyl)-1,3-propane diamine, b) a fatty monoamine of formula M_a , wherein R_2 is a hydrocarbyl group with 12-18 carbon atoms, and c) a hydrophilic polysaccharide.

5

11. A process according to claim 10 wherein component c) is starch.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2007/064157

A. CLASSIFICATION OF SUBJECT MATTER

INV. B03D1/01
ADD. B03D1/008 B03D1/016 B03D103/04 B03D101/02

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)
B03D

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

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 076 682 A (GUSTAFSSON JAN OLOF [SE] ET AL) 20 June 2000 (2000-06-20) cited in the application column 3, line 59 - line 62 column 2, line 1 - line 64 column 2, line 29 - line 39 claims 1-8	1-11
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Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

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

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

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the International search

11 April 2008

Date of mailing of the international search report

28/04/2008

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Roider, Josef

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2007/064157

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 697 744 A (WADA MINORU [JP] ET AL) 6 October 1987 (1987-10-06) col umn 3, line 57 - column 4, line 15 col umn 6, line 56 - line 58 col umn 7, line 32 - line 41 col umn 14, line 1; example 6 cl aims 1,4, 10 -----	
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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2007/064157

(^Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2 987 183 A (BISHOP WILLIAM T) 6 June 1961 (1961-06-06) column 1, line 56 - column 2, line 2; example 3 -----	1-11
Y	US 3 273 707 A (MALTBY, P.D.R.) 20 September 1966 (1966-09-20) column 1, line 10 - line 31 column 2, line 6 - line 8; claim 1 -----	1-11
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP2007/064157

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. As all required additional search fees were timely paid by the applicant, this international search report covers allsearchable claims.
2. As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
3. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM POT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1 (part), corresponding parts of claims 2-11

Group I is directed to a reverse froth flotation process with a collector comprising a mixture of C12-C15 alkyl ether diamines and C12-C24 alkyl monoamines.

2. claims: 1 (part), corresponding parts of claims 2-11

Group II is directed to a reverse froth flotation process with a collector comprising a mixture of C12-C15 alkyl ether diamines and C12-C24 alkyl ether monoamines.

3. claims: 1 (part), corresponding parts of claims 2-11

Group III is directed to a reverse froth flotation process with a collector comprising a mixture of C12-C15 alkyl ether diamines and C16-C24 alkyl diamines.

4. claims: 1 (part), corresponding parts of claims 2-11

Group IV is directed to a reverse froth flotation process with a collector comprising a mixture of alkyl ether diamines having C12-C15 and C16-C24 alkyl groups.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2007/064157

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