INSTRUCTIONS

(a) If Convention application insert "Convention"

(a) Convention

AUSTRALIA **593065**

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(b) Delete one

APPLICATION FOR A (b) STANDARD ~~PETTY~~ PATENT

PATENT OFFICE

I/We (c) L'AIR LIQUIDE, SOCIETE ANONYME POUR L'ETUDE ET L'EXPLOITATION DES PROCEDES GEORGES CLAUDE

of (d) 75 quai d'Orsay - 75007 PARIS (FRANCE)

hereby apply for the grant of a (c) Standard/~~Petty~~ Patent for an invention entitled

(f) "PROCESS FOR ENRICHING SULPHIDE ORE"

which is described in the accompanying (g) complete specification.

(Note: The following applies only to Convention applications)

Details of basic application(s)

(h) Insert number, country and filing date for the/or each basic application

	Application No.	Country	Filing Date
(h)	86.02.784	FRANCE	February 28, 1986

APPLICATION ACCEPTED AND AMENDMENTS ALLOWED 21-11-89

Address for Service

26 FEB 1987 Melbourne

PHILLIPS ORMONDE AND FITZPATRICK
Patent and Trade Mark Attorneys
367 Collins Street
Melbourne, Australia 3000

(i) Insert date of signing

Dated (i) February 20, 1987

(j) Signature of applicant(s) (For body corporate see headnote*)

(j)

Eric GEORGES-PICOT
Directeur des Services Administratifs

L'AIR LIQUIDE Société Anonyme pour l'Etude et l'Exploitation des Procédés GEORGES CLAUDE 75, Quai d'Orsay PARIS

(k) Corporate seal if any

(k)

Note: No legalization or other witness required

FEE STAMP TO VALUE OF $150 ATTACHED
MAIL OFFICER

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Melbourne, Australia

P17/2/83

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DECLARATION FOR A PATENT APPLICATION

▼ **INSTRUCTIONS**

(a) Insert "Convention" if applicable

(b) Insert FULL name(s) of applicant(s)

In support of the (a) convention application made by (b) AIR LIQUIDE, SOCIETE ANONYME POUR L'ETUDE ET L'EXPLOITATION DES PROCEDES GEORGES CLAUDE

(c) Insert "of addition" if applicable

(d) Insert TITLE of invention

(hereinafter called "applicant(s)" for a patent (c) for an invention entitled (d)

"PROCESS FOR ENRICHING SULPHIDE ORE"

(e) Insert FULL name(s) AND address(es) of declarant(s) (See headnote*)

I/We Eric GEORGES- PICOT
of L'AIR LIQUIDE, SOCIETE ANONYME POUR L'ETUDE ET L'EXPLOITATION DES PROCEDES GEORGES CLAUDE - 75 quai d'Orsay - 75007 PARIS (FRANCE)

do solemnly and sincerely declare as follows:

1. I am/We are the applicant(s).

(or, in the case of an application by a body corporate)

1. I am/We are authorized to make this declaration on behalf of the applicant(s).
2. I am/We are the actual inventor(s) of the invention.

(or, where the applicant(s) is/are not the actual inventor(s))

(f) Insert FULL name(s) AND address(es) of actual inventor(s)

2. (f) Gérard DECLERCK of 8, rue Bizanet - 38000 GRENOBLE (FRANCE) ;
Bruno GARNIER of 26, rue Général Ferié - 38100 BRENOBLE (FRANCE) ;
PIerre KARINTHI of 66, rue Anatole France - 78350 JOUY-EN-JOSAS (FRANCE) ;
Alain TRICHET of 9, avenue Alsace-Lorraine - 38000 GRENOBLE (FRANCE) ;
Jean-Luc CECILE of Les Fours à Chaux - DRACY - 89130 TOUCY (FRANCE).
is/are the actual inventor(s) of the invention and the facts upon which the applicant(s) is/are entitled to make the application are as follows:

(g) Recite how applicant(s) derive(s) title from actual inventor(s) (See headnote**)

(g)
The applicant is the assignee of the invention from the actual inventors

(Note: Paragraphs 3 and 4 apply only to Convention applications)

(h) Insert country, filing date, and basic applicant(s) for the/or EACH basic application

3. The basic application(s) for patent or similar protection on which the application is based is/are identified by **country, filing date, and basic applicant(s)** as follows:

(h)
FRANCE, filed on February 28, 1986 under N° 86.02.784
by L'AIR LIQUIDE, SOCIETE ANONYME POUR L'ETUDE ET L'EXPLOITATION DES PROCEDES GEORGES CLAUDE

4. The basic application(s) referred to in paragraph 3 hereof was/were the first application(s) made in a Convention country in respect of the invention the subject of the application.

(k) Insert PLACE of signing

(l) Insert DATE of signing

(m) Signature(s) of declarant(s)

Note: No legalization or other witness required

Declared at (k) Paris

Dated (l) February 20, 1987

(m) _____

Eric GEORGES-PICOT

Directeur des Services Administratifs

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To: The Commissioner of Patents

P18/7/78

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(12) PATENT ABRIDGMENT (11) Document No. AU-B-69283/87
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 593065

(54) Title
PROCESS FOR ENRICHING SULPHIDE ORE

International Patent Classification(s)
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86 02784	**28.02.86**	**FR FRANCE**

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(74) Attorney or Agent
PHILLIPS,ORMONDE & FITZPATRICK

(57) Claim

1. A process for enriching an ore including a plurality of metallic sulphides, comprising effecting a wet crushing of the ore, then subjecting the pulp obtained to a conditioning operation and then a flotation operation so as to create a plurality of floating products each of which is richer in one of the metallic sulphides than the initial ore, wherein the redox potential of the pulp is maintained substantially constant during the conditioning operation and wherein the crushing operation is carried out under an inert protective atmosphere so as to avoid the oxidation of the surfaces which are freshly created during said crushing operation.

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COMPLETE SPECIFICATION
(ORIGINAL)

Class Int. Class

Application Number: 69283/87
Lodged:

Complete Specification Lodged:
Accepted:
Published:

Priority

Related Art:

This document contains the amendments made under Section 49 and is correct for printing.

APPLICANT'S REFERENCE: SERIE: 2850/221/07

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Complete Specification for the invention entitled:

PROCESS FOR ENRICHING SULPHIDE ORE

Our Ref : 47270
POF Code: 1290/43509

The following statement is a full description of this invention, including the best method of performing it known to applicant(s):

PROCESS FOR ENRICHING SULPHIDE ORE

The present invention relates to a process for enriching an ore including a plurality of metallic sulphides comprising effecting a wet crushing of the ore, the pulp obtained being then subjected to conditioning and then flotation operations so as to create a plurality of floating products each of which is richer in one of the metallic sulphides than the initial ore.

In its principle, flotation comprises entraining certain solid particles by the clinging of gas bubbles to their surfaces in order to separate them from other particles to which there is no clinging of the bubbles. This operation is carried out in the presence of water and the surface of the particles which are required to float must be rendered hydrophobic, i.e. their wettability by water must be low.

When the surface of the particles which are required to float is not sufficiently hydrophobic, a reagent termed a collector is added to the solution in order to reinforce this hydrophobic character, this collector being adsorbed on certain surfaces and thus rendering them more hydrophobic, i.e. water repellent, which then enables the gases to cling to the surface of the particles and cause the flotation of the latter. As the floating product is collected in the upper part of the flotation vessel in the form of froth, a foaming agent is added to the pulp to stabilize it.

In the field of the treatment of sulphide ores, one seeks to achieve a selectivity of separation of the various

metallic sulphides contained in the initial ore. To achieve this selectivity, there must be a difference in the degree of wettability of the solid components of the ore. This difference of wettability is created or strengthened by the addition of various modifying agents:

depressing agents which reinforce the hydrophilic character of certain constituents of the ore,

activating agents which reinforce the action of the collector.

All of the reagents are generally added in a conditioning tank located on the upstream side of the flotation vessels during an operation termed conditioning.

The technique of selective separation of the ores by conditioning-flotation is effectively applicable solely to ores whose particles have been crushed sufficiently finely to release the ores present. During this crushing, usually carried out in the presence of a liquid phase and the air of the atmosphere, fresh surfaces are created by the fragmentation of the grains. Now, it has been found that, owing to the fact that these operations are carried out in the air of the atmosphere, the freshly-crushed surfaces are the centre of a certain number of reactions. These surfaces modified in this way will be acted upon by the various reagents in the conditioning and flotation stages.

For example, when copper sulphides - mainly chalcopyrite - are separated from the blende, and although the blende does not float under the normal conditions of flotation of

the chalcopyrite, the uncontrolled formation of a layer of copper sulphide on the surface of the grains of blende renders the flotation of the latter possible (phenomenon of the activation of the blende). In order to overcome these effects, "de-activating" products are added to the pulp which avoid the formation of the surface layer of copper sulphide, for example $ZnSO_4$, SO_2, NaCN, S^{--}, each de-activating product acting in accordance with a particular mechanism. This therefore requires the use of rather expensive reagents and presents problems of environment.

The process according to the invention avoids these drawbacks. For this purpose, it is characterised in that the crushing operation is carried out under an inert protective atmosphere in order to avoid oxidation of the surfaces freshly created during this operation, and the redox potential of the pulp during the conditioning is maintained substantially constant.

~~Preferably, the redox potential is maintained constant~~ by the injection of nitrogen and/or oxidizing gas.

The use of a gaseous atmosphere different from that of air in the crusher, but also in the conditioner, enables the conditioning and flotation vessels to be fed with an ore whose surface is different from that existing during the conventional procedure in air. This is used in order to improve the separation of the ores from one another.

An improved control of the crushing, conditioning and ~~flotation operations is in this way achieved by a closer~~

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Preferably, the redox potential is maintained constant by the injection of nitrogen and/or oxidizing gas. The redox potential may be less than -200 mV. Preferably the redox potential is greater than -500 mV.

The use of a gaseous atmosphere different from that of air in the crusher, but also in the conditioner, enables the conditioning and flotation vessels to be fed with an ore whose surface is different from that existing during the conventional procedure in air. This is used in order to improve the separation of the ores from one another.

An improved control of the crushing, conditioning and flotation operations is in this way achieved by a closer

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control of the state of oxidation of the surfaces of the ores.

As advantages of this process, in addition to the fact of having in certain cases the additional possibility of variation of a parameter which may permit separations heretofore impossible in the art, there have been obtained an improvement in the selectivity of separation of the ores, a reduction in the consumption of the reagents and consequently a reduction in pollutions due to the liquid rejects.

~~Preferably,~~ Inert atmospheres will be employed during the crushing so as to eliminate or highly reduce any phenomenon of oxidation of the surfaces freshly created during this operation. During the subsequent conditioning operation, the redox potential of the pulps will be regulated by the alternating injection of nitrogen and/or oxygen or nitrogen and/or a gaseous mixture including oxygen, so as to obtain the best conditions for the selectivity of separation of the ores.

~~A further advantage is the reduction in the consumption~~ of the crushing members (usually balls) owing to a reduction in the corrosion.

In the case of the blende, for example, although the basic reaction of its activation is an ion exchange reaction, the applicant believes that oxidation mechanisms control the development thereof, for example in respect of the generation of the cu^{++} ions - the latter coming from the dissolving of the copper of the chalcopyrite which depends on the

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of the ores. Suitable inert protective atmospheres can be obtained by means of a gas selected from nitrogen argon and/or carbon dioxide.

A further advantage is the reduction in the consumption of the crushing members (usually balls) owing to a reduction in the corrosion.

In the case of the blende, for example, although the basic reaction of its activation is an ion exchange reaction, the applicant believes that oxidation mechanisms control the development thereof, for example in respect of the generation of the cu^{++}ions - the latter coming from the dissolving of the copper of the chalcopyrite which depends on the

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oxidation of the latter.

The use of controlled atmospheres in this specific case results in an improvement in the selectivity of copper-zinc separation while reducing the consumption of reagents.

Generally, the process according to the invention comprises, during the wet crushing of the ore, maintaining an inert atmosphere in the crusher by the injection of nitrogen. If desired, this injection will also be effected in the water fed to the pulp for the purpose of de-aerating it.

This rendering of the atmosphere inert is maintained during the transfer of the pulp to the conditioner. During conditioning, the redox potential of the pulp is maintained substantially constant at the desired values by successive additions of nitrogen (for lowering the redox potential) and oxygen - or an oxidizing gas - (for increasing it). The same procedure may be adopted in respect of the flotation proper.

The industrial applications of the invention concern generally the treatment of sulphide ores. A sector of interest is more particularly the improvement of the copper-zinc selectivity. The invention also concerns the treatment of complex sulphide ores and oxidized sulphide ores such as argentiferous or auriferous ores having a sulphide gangue.

A better understanding of the invention will be had from the following description of modes of carrying out the invention given by way of non-limiting examples:

Tests were carried out in the laboratory on mixtures of

copper sulphide ores (the specimen comprising principally chalcopyrite with the presence of chalcosine or digenite) and zinc (sphalerite) with the following procedures.

Crushing procedure:

In a ball crusher there is crushed a mixture of the chalcopyrite specimen (18 grams), blende (32 grams) and quick lime (1 gram) with quartz (about 500 grams) in the presence of 250 ml of water. The duration of the operation is 50 minutes. At the end of the crushing, a pulp is obtained whose solids have a d_{50} less than 64 μ and a d_{80} less than 96 μ ($d_{50} < 64\ \mu$ signifies that at least 50% of the solids have a diameter of less than 64 μ and $d_{80} < 96\ \mu$ that at least 80% have a diameter of less than 96 μ). Preferably, the $d_{50\%}$ is $20\ \mu < d_{50\%} < 200\ \mu$.

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~~copper sulphide ..es (the specimen comprising principally~~ chalcopyrite with the presence of chalcosine or digenite) and zinc (sphalerite) with the following procedures.

Crushing procedure:

In a ball crusher there is crushed a mixture of the chalcopyrite specimen (18 grams), blende (32 grams) and quick lime (1 gram) with quartz (about 500 grams) in the presence of 250 ml of water. The duration of the operation is 50 minutes. At the end of the crushing, a pulp is obtained whose solids have a d_{50} less than 64 µ and a d_{80} less than 96 µ ($d_{50} < 64$ µ signifies that at least 50% of the solids have a diameter of less than 64 µ and $d_{80} < 96$ µ ~~that at least 80% have a diameter of less than 96 µ).~~

Conditioning procedure:

After decantation in the conditioner, the volume of the pulp issuing from the crusher is brought back to 1 litre.

The pulp is conditioned by the introduction of the following reagents having a pH of 8.5:

collector: potassium ethylxanthate 70 mg/kg

foaming agent: methylisobutylcarbinol 2 mg/kg

The conditioning time is set at 15 minutes.

during the conditioning, the redox potential is maintained by regulation at a fixed value by successive additions of nitrogen and oxygen in the Examples 2 to 5. In Example 1, no gas is injected.

First flotation:

It is carried out in a DENVER D 12 vessel. During this

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first flotation, the chalcopyrite must be recovered in the floating concentrate which is skimmed off for three minutes. The rate of flow of the gas (Examples 2 to 5 - nitrogen) injected on the axis of the turbine is 180 l/h. The turbine rotates at 1,200 rpm.

Second conditioning :

The pulp is then activated by the introduction of 0.25 g of CuS04 - 5 H20 so as to cause the blende to float. The duration of the absorption of the Cu^{2+} ions is set at 5 minutes.

A second conditioning is then carried out with a collector and foaming agent which are identical to those of the first conditioning.

Second flotation:

during this flotation, the blende which had been activated during the second conditioning must be essentially recovered. The hydrodynamic conditions are identical to those of the first flotation.

EXAMPLE 1

Crushing in air,

Pulp potential non-regulated during the conditionings and flotations,

pH - 8.5

Addition of Zn SO4 - 500 $g.t^{-1}$ during the first conditioning.

	COPPER	ZINC
Initial content (%)	0.85	2.01
Content in the floating product 1 (%)	11.31	27.37
Distributivity in the floating product 1 (%)	93.77	96.48
Content in the floating product 2 (%)	0.69	0.68
Distributivity in the floating product 2 (%)	3.11	1.30

There is found in the floating product 1 the same copper-zinc proportion as in the initial ore - no separation had been achieved. This reference test is characterised in that the various crushing, conditioning and flotation operations are carried out in air and the redox potential is not controlled during the conditioning.

During the first conditioning, there is added in addition to the collector (potassium ethylxanthate) and the foaming agent (methylisobutylcarbinol), zinc sulphate in a large amount (500 g/ton) in order to avoid or eliminate the activation of the blende.

EXAMPLES 2 AND 3

Crushing in air,

Redox potential of the pulp regulated during the conditioning at -350 mV S.C.E. by injection of nitrogen and oxygen into the pulp,

pH = 8.5

Example 2

	COPPER	ZINC
Initial content (%)	1.03	2.20
Content in the floating product 1 (%)	8.32	29.72
Distributivity in the floating product 1 (%)	43.65	73.15
Content in the floating product 2 (%)	12.21	15.63
Distributivity in the floating product 2 (%)	28.62	17.19

There is found a slight increase in the proportion of zinc in the floating product 1 relative to the copper, with an inverse proportion in the floating product 2.

Example 3

	COPPER	ZINC
Initial content (%)	0.96	2.24
Content in the floating product 1 (%)	11.39	31.00
Distributivity in the floating product 1 (%)	76.87	89.64
Content in the floating product 2 (%)	8.66	16.47
Distributivity in the floating product 2 (%)	8.67	7.66

These tests were carried out with crushing in air and a control of the redox potential.

The conditioning operations are carried out with a control of the pulp potential by the addition of N2 and O2 gas

and with additions of collector (potassium ethylxanthate) and foaming agent (methylisobutylcarbinol) such as described before. The flotation operations are carried out with injection of nitrogen on the axis of the turbine.

The expected selectivity separation of the copper relative to the zinc was not obtained. It even appears that there was an enrichment in the content of zinc in the floating product 1. The distributivities of the copper and zinc however remain close to each other.

EXAMPLES 4 and 5:

Crushing under nitrogen,

Pulp potential regulated during the conditioning at -350 mV S.C.E. by the injection of nitrogen and oxygen,

pH = 8.5

Example 4

	COPPER	ZINC
Initial content (%)	0.91	2.02
Content in the floating product 1 (%)	8.83	6.70
Distributivity in the floating product 1 (%)	59.81	20.63
Content in the floating product 2 (%)	7.90	31.12
Distributivity in the floating product 2 (%) (relative to the initial content)	32.25	57.08

It is found that in the floating products 1, an enrichment in copper was achieved (the ratio of the Cu/Zn contents

is equal to 1.3 as against 0.45 in the incoming ore). About 60% copper and only 21% zinc are recovered at these contents in the concentrate 1. An excellent separation of the sulphides and of the zinc and copper is therefore achieved.

Example 5

	COPPER	ZINC
Initial content (%)	0.96	2.08
Content in the floating product 1 (%)	22.46	17.70
Distributivity in the floating product 1 (%)	48.97	17.84
Content in the floating product 2 (%)	7.46	35.81
Distributivity in the floating product 2 (%)	31.54	69.99

It is found that the same advantages as in Example 4 are obtained. The contents of the concentrate 1 are higher than in Example 4, the ratio of the Cu/Zn contents remains at about 1.3. An excellent separation of the zinc and copper sulphides is therefore achieved.

These tests were carried out with crushing in nitrogen and a control of the redox potential.

The operational protocol is the same as in Examples 2 and 3 for the conditionings and the flotations. On the other hand, the crushing is carried out under a nitrogen atmosphere.

The claims defining the invention are as follows:

1. A process for enriching an ore including a plurality of metallic sulphides, comprising effecting a wet crushing of the ore, then subjecting the pulp obtained to a conditioning operation and then a flotation operation so as to create a plurality of floating products each of which is richer in one of the metallic sulphides than the initial ore, wherein the redox potential of the pulp is maintained substantially constant during the conditioning operation and wherein the crushing operation is carried out under an inert protective atmosphere so as to avoid the oxidation of the surfaces which are freshly created during said crushing operation.

2. A process according to claim 1 wherein the redox potential is maintained constant by the injection of nitrogen and/or oxidizing gas.

3. A process according to any one of claims 1 or 2 wherein the inert protective atmosphere is obtained by means of a gas selected from nitrogen, argon and/or carbon dioxide.

4. A process according to any one of the claims 1 to 3 wherein the redox potential is less than -200 mV.

5. A process according to any one of the claims 1 to 4 wherein the redox potential is greater than -500 mV.

6. A process according to any one of the claims 1 to 5 wherein the crushing operation produces particles whose diameter $d_{50\%}$ is such that: $20\ \mu < d_{50\%} < 200\ \mu$.

7. A process for enriching an ore including a plurality of metallic sulphides, substantially as hereinbefore described with reference to Example 4 or 5.

DATED: 15 November 1989.

PHILLIPS ORMONDE & FITZPATRICK

Attorneys for:

L'AIR LIQUIDE, SOCIETE ANONYME POUR L'ETUDE ET L'EXPLOITATION DES PROCEDES GEORGES CLAUDE

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