

INSTRUCTIONS

(a) If Convention application insert "Convention"

(a) Convention
593065
AUSTRALIA

Patents Act

(b) Delete one

APPLICATION FOR A (b) STANDARD/~~UTILITY~~ PATENT

~~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 (e) Standard/~~Utility~~ 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)

PATENT OFFICE

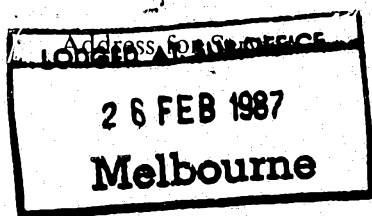


(h) Insert number, country and filing date for the/or each basic application

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

APPLICATION ACCEPTED AND AMENDMENTS

ALLOWED 21-11-89



PHILLIPS ORMONDE AND FITZPATRICK
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Dated (i) February 20, 1987

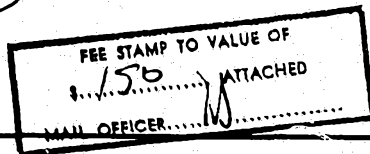
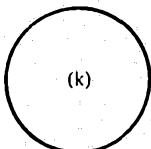
(i) Insert date of signing

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

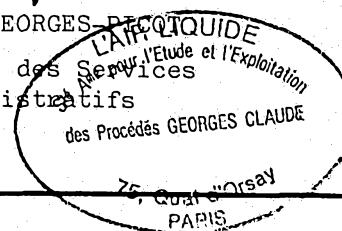
(j)

(k) Corporate seal if any

Note: No legalization or other witness required



Eric GEORGES-DEQUOIDE
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DECLARATION FOR A PATENT APPLICATION

▼ INSTRUCTIONS

(a) Insert "Convention" if applicable
(b) Insert FULL name(s) of applicant(s)

(c) Insert "of addition" if applicable
(d) Insert TITLE of invention

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

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

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

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

(k) Insert PLACE of signing

(l) Insert DATE of signing

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

Note: No legalization or other witness required

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

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

"PROCESS FOR ENRICHING SULPHIDE ORE"

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. ~~X I am/WE are the actual inventor(s) of the invention~~
(or, where the applicant(s) is/are not the actual inventor(s))
2. (i) 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)
The applicant is the assignee of the invention from the actual inventors

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

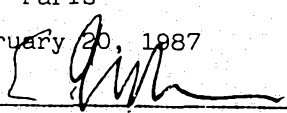
3. The basic application(s) for patent or similar protection on which the application is based
is/are identified by country, filing date, and basic applicant(s) as follows:

(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.

Declared at (k) Paris

Dated (l) February 20, 1987

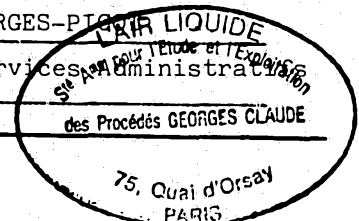
(m) 
Eric GEORGES-PICOT

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)
(51)⁴ **B03D 001/06**

(21) Application No. : **69283/87** (22) Application Date : **26.02.87**

(30) Priority Data

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86 02784	28.02.86	FR FRANCE

(43) Publication Date : **03.09.87**

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PROCEDES GEORGES CLAUDE**

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(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.

593065

AUSTRALIA

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COMPLETE SPECIFICATION
(ORIGINAL)

Application Number: 69283/87
Lodged:

Class

Int. Class

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
5 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.

10 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
15 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
20 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
25 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
5 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.

10 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
15 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
20 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.

25 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 chalcopryite, 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



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.

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



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.

10 ~~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
15 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~~
20 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
25 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



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



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.

5 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.

10 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
15 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
20 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
25 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 chalcopryrite 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 chalcopryrite 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 64μ and a d_{80} less than 96μ ($d_{50} < 64 \mu$ signifies that at least 50% of the solids have a diameter of less than 64μ and $d_{80} < 96 \mu$ that at least 80% have a diameter of less than 96μ). Preferably, the $d_{50\%}$ is $20 \mu < d_{50\%} < 200 \mu$.



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chalcopryrite with the presence of chalcosine or digenite)
and zinc (sphalerite) with the following procedures.

Crushing procedure:

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chalcopryrite 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 obtai-
10 ned whose solids have a d_{50} less than 64μ and a d_{80} less
than 96μ ($d_{50} < 64 \mu$ signifies that at least 50% of the so-
lids have a diameter of less than 64μ and $d_{80} < 96 \mu$
~~that at least 80% have a diameter of less than 96μ).~~

Conditioning procedure:

- 15 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 fol-
lowing reagents having a pH of 8.5:

collector: potassium ethylxanthate 70 mg/kg

- 20 foaming agent: methylisobutylcarbinol 2 mg/kg

The conditioning time is set at 15 minutes.

- during the conditioning, the redox potential is maintai-
ned by regulation at a fixed value by successive additions
of nitrogen and oxygen in the Examples 2 to 5. In Example
25 1, no gas is injected.

First flotation:

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



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
5 rotates at 1,200 rpm.

Second conditioning :

The pulp is then activated by the introduction of 0.25 g of $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ so as to cause the blende to float. The duration of the absorption of the Cu^{2+} ions is set at 5
10 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:

15 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

20 Crushing in air,

Pulp potential non-regulated during the conditionings and flotations,

pH - 8.5

Addition of $\text{Zn SO}_4 - 500 \text{ g.t}^{-1}$ during the first condi-
25 tioning.

	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

10 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
15 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
20 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,
25

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.

- 5 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.

10 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

15 Example 4

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

25

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.

5 Example 5

	COPPER	ZINC
Initial content (%)	0.96	2.08
Content in the floating product 1 (%)	22.46	17.70
Distributivity in the		
10 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

15 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.

20 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 at-
25 mosphere.

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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