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NOTICE OF ENTITLEMENT

We TECHNOLOGICAL RESOURCES PTY LTD
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MELBOURNE, VICTORIA 3000
AUSTRALIA

being the applicant in respect of an application for a patent for an invention entitled
REGENERATION OF HYDROCHLORIC ACID (Application No.29361/92), state the
following:

1. The nominated person has, for the following reasons, gained entitlement from the actual inventors:

by Deed of Assignment
2. The nominated person has entitlement from the applicants of the application listed in the declaration under Article 8 of the PCT by virtue of being the assignee of the said inventors.
3. The application listed in the declaration made under Article 8 of the PCT is the first application made in a Convention country in respect of the invention.

DATE: 20 July 1993

TECHNOLOGICAL RESOURCES PTY LTD
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Patent Attorney for and
on behalf of the applicant



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REGENERATION OF HYDROCHLORIC ACID
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- (71) Applicant(s)
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- (56) Prior Art Documents
AU 436122 57744/69
AU 13262/91
AU 26104/77
- (57) Claim

1. **A process for forming an aqueous chloride leachant from a spent aqueous chloride leach liquor which process comprises the steps of:**
- a) **passing a spent aqueous chloride leach liquor and gases containing hydrogen chloride through a preconcentrator to form a concentrated aqueous chloride leach liquor by partial evaporation of water therefrom and absorption of hydrogen chloride**
 - b) **withdrawing a portion of the concentrated aqueous chloride leach liquor;**
 - c) **roasting the remainder of the concentrated aqueous chloride leach liquor to generate a metal oxide and gases containing hydrogen chloride and water vapour therefrom;**

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d) passing the gases containing hydrogen chloride to step a); and

e) recovering hydrogen chloride exiting the preconcentrator by dissolving it in water to form regenerated hydrochloric acid.

8. Apparatus for forming an aqueous chloride leachant from a spent aqueous chloride leach liquor, the apparatus comprising preconcentrator means for evaporating water from the spent aqueous chloride leach liquor and contacting it with gases containing hydrogen chloride; extraction means for extracting concentrated aqueous leach liquor from the preconcentrator means and dividing it into first and second portions of concentrated aqueous chloride leach liquor; roasting means for roasting the second portion of concentrated aqueous chloride leach liquor to produce a metal oxide and gases containing hydrogen chloride; absorption means for absorbing hydrogen chloride in water; first conduit means for conducting gases generated in the roasting means to the preconcentrator means; second conduit means for conducting gases exiting from the preconcentrator means to the absorption means; and third conduit means for conducting the first portion of concentrated aqueous chloride leach liquor from the extraction means the third conduit means having a valve to control the flow of the first portion of concentrated aqueous chloride leach liquor.

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<p>(21) International Application Number: PCT/AU92/00625 (22) International Filing Date: 23 November 1992 (23.11.92) (30) Priority data: PK 9653 22 November 1991 (22.11.91) AU (71) Applicant (for all designated States except US): TECHNOLOGICAL RESOURCES PTY LIMITED [AU/AU]; A.C.N. 002 183 557, Level 39, 55 Collins Street, Melbourne, VIC 3001 (AU). (72) Inventors; and (75) Inventors/Applicants (for US only) : HOLLITT, Michael, John [AU/AU]; McLelland, Ross, Alexander [AU/AU]; Wimmera Industrial Minerals Pty Limited, 2nd Floor, 15 Bank Street, South Melbourne, VIC 3205 (AU).</p>		<p>(74) Agent: GRIFFITH HACK & CO.: 3rd Floor, 509 St Kilda Road, Melbourne, VIC 3004 (AU). (81) Designated States: AT, AU, BB, BG, BR, CA, CH, CS, DE, DK, ES, FI, GB, HU, JP, KP, KR, LK, LU, MG, MN, MW, NL, NO, PL, RO, RU, SD, SE, UA, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, SN, TD, TG). Published With international search report. 663130</p>
<p>(54) Title: REGENERATION OF HYDROCHLORIC ACID (57) Abstract The specification discloses a process for regenerating aqueous chloride leach liquors. The process involves roasting aqueous chloride leach liquor to produce metal oxide and a gas containing HCl. The gas containing HCl is passed through a preconcentrator where it is contacted with spent aqueous chloride leach liquor. The enthalpy of the gas evaporates water from the spent liquor thereby concentrating it. At the same time the spent liquor absorbs HCl. HCl not absorbed in the preconcentrator is contacted with water to form hydrochloric acid. The hydrochloric acid may be mixed with the concentrated spent liquor and re-used. Apparatus for operating the process is also disclosed.</p>		

REGENERATION OF HYDROCHLORIC ACID

The present invention relates to the regeneration of hydrochloric acid used in processing ores to recover mineral products therefrom.

Sulphuric acid has been the acid most commonly used in the leaching and digestion of ores for the recovery of mineral products therefrom. Principally this is related to the low cost of sulphuric acid manufacture and use and the ease with which sulphuric acid could be transported from the point of production to the point of use. However, with the development of acid resistant plastics, it became feasible to transport hydrochloric acid, which for some applications is more suitable for the leaching and digestion of ores for the recovery of mineral products therefrom.

The development of a spray roasting process for recovering hydrochloric acid from spent leach liquors has given added impetus to the use of hydrochloric acid in hydrochemical treatment of ores for the recovery of mineral products. The spray roasting process is described in "Hydrochloric Acid Regeneration", as distributed by Babcock Contractors Limited. Essentially the process involves passing spent aqueous chloride leach liquors through a preconcentrator to form a concentrated spent aqueous chloride liquor by partial evaporation of water therefrom and spray roasting the concentrated aqueous chloride leach liquor to generate a metal oxide, hydrogen chloride and water vapour therefrom. Spray roaster gases are cooled by direct contact with chloride liquors in the preconcentrator. The hydrogen chloride gas exiting the preconcentrator is recovered by absorption in water to form regenerated hydrochloric acid which can then be used to leach or digest more ore. Normally

the hydrogen chloride evolved from the spray roaster is absorbed in water in a countercurrent absorption column. The water used may be filter cake wash water, although only if weak in chloride strength. In this regeneration process only those quantities of hydrochloric acid that are lost due to the formation of chlorides that cannot be thermally decomposed have to be replaced by fresh hydrochloric acid. Chlorides that cannot be thermally decomposed include some alkaline and alkaline earth metal chlorides.

Spray roasting is often performed in a tower. Spent liquor is sprayed in at the top of the tower through one or more nozzles. Hot gases generated by combustion of oil or natural gas in burners located externally of the tower are blasted tangentially into the tower thus producing a rotational flow inside the tower. Initially water evaporates from the droplets formed by the nozzles as the droplets fall through the tower. As the chloride solution becomes more concentrated chloride crystals form which ultimately decompose into water vapour, hydrogen chloride and metal oxide. A typical equation for the decomposition of chlorides in this way can be written as follows:-



where M is a divalent metal.

In other arrangements spray roasting is conducted in a fluidised bed.

Gases evolved from the spray roaster are then passed through the preconcentrator which normally consists of either

- a packed column through which the gases evolved by the spray roaster pass upwardly

and spent liquid is introduced at the top of the tower and flows downwardly into the spray roaster, or

- a void tower in which cocurrent contact of gas and liquid is encouraged.

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In this way heat from the spray roasting step is used to concentrate the spent liquor before it passes to the spray roaster thereby improving the energy efficiency of the total process.

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The method of operation of spray roasting as described and commonly operated, eg. for acid recovery from steel pickling liquors or from ilmenite leach liquors, results in a maximum recycled acid strength equivalent to the azeotrope. Since the azeotrope occurs at an acid strength of 20 wt % HCl, four units of water per unit of HCl must be added into the absorber to be recycled in the acid. That is, the minimum water evaporation requirement in regeneration of used acid is four units per unit of useful HCl. The high heat input requirements in spray roasting for this water evaporation renders acid regeneration uneconomical for many potential applications and is a major commercial disincentive for the use of hydrochloric acid in leach processing. Alternative schemes for the production and use of superazeotropic acid require concentration of chloride liquors by evaporation prior to acid regeneration, with little or no saving in energy costs. Such schemes are not favoured where superazeotropic acid is not required, as is the case for most applications.

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Hydrochloric acid has been used in the production of synthetic rutile from ilmenite and other titaniferous materials by a number of leach processes at both commercial

and pilot scales. The processes typically may involve the following steps:-

1. Oxidatively roasting ilmenite.
- 5 2. Reducing the product of step 1 at elevated temperature.
3. Cooling the product of step 2.
4. Digesting the cooled product of step 2 in hydrochloric acid.
5. Filtering the product of step 4 to produce filtrate and
10 filter cake.
6. Recovering synthetic rutile from the filter cake.
7. Spray roasting the filtrate to recover hydrochloric acid and generate iron oxide for disposal or sale.

15 An article by H N Sinha of CSIRO (in Titanium '80: Science and Technology, TMS-AIME, New York, 1980, Vol. 3) demonstrates that the addition of ferrous chloride to hydrochloric acid has a beneficial effect on the leaching rate, the production of fines and in the amount of water in
20 the leach liquor. The article also suggests that this information could be used to improve the Murso process by splitting the leach liquor into two streams, one going for regeneration of 20% HCl and the other being recycled and mixed with the regenerated acid to make up the leachant after
25 first undergoing a concentration step to remove excess water. Such a scheme does not significantly reduce the water evaporation requirements in acid regeneration, however.

It has now been discovered that the economics of acid
30 regeneration and formation of leachant can be significantly improved by extracting concentrated spent liquor from the preconcentrator of the usual spray roasting equipment rather than separating the spent liquor streams into one stream passing through the spray roaster and the other through a

concentrator.

It is the object of the present invention to provide a means for the regeneration of hydrochloric acid used in leach/digestion circuits, for which the following are requirements:

(i) Process water evaporation requirements should be substantially less than the water addition which would be required to absorb regenerated hydrogen chloride into water as sub azeotropic acid.

(ii) Spent leach liquors are used for absorption of a proportion of regenerated hydrogen chloride and transport of hydrochloric acid back to leach.

Accordingly, the present invention provides a process for forming an aqueous chloride leachant from a spent aqueous chloride leach liquor which process comprises passing a spent aqueous chloride leach liquor and gases containing hydrogen chloride through a preconcentrator to form a concentrated aqueous chloride leach liquor by partial evaporation of water therefrom and absorption of hydrogen chloride; withdrawing a portion of the concentrated aqueous chloride leach liquor; roasting the remainder of the concentrated aqueous chloride leach liquor to generate a metal oxide, and gases containing hydrogen chloride; and passing the gases containing hydrogen chloride to the preconcentrator.

Gases evolved from the preconcentrator may be contacted with water in an absorber to remove hydrogen chloride therefrom. The resultant hydrochloric acid may be mixed with the withdrawn portion of concentrated aqueous chloride leach liquor.

Since the concentrated spent aqueous chloride leach liquor contains hydrochloric acid absorbed from spray roaster exit gases this acid may be used in leaching without the need to
5 add new water for absorption. Overall the need to add and then evaporate water is reduced.

Preferably the leach liquor is one derived from operation of a leach or pickling process in which case the spent leach
10 liquor largely comprises an aqueous solution of metal chlorides.

In the simplest arrangement existing equipment used for practising the regeneration process can be adapted to the
15 process of the present invention simply by installing an outlet and a control valve at the bottom of the preconcentrator to remove concentrated aqueous chloride leach liquor containing absorbed hydrochloric acid for mixing with regenerated hydrochloric acid and return to
20 leaching/digestion.

The alternative proposed by Sinha would involve the incorporation of a second concentrator, the use of additional heating apparatus for the second concentrator as well as
25 additional pipework. Further, the Sinha proposal does not reduce absorption water inputs or evaporation requirements, as virtually all recycled acid is absorber acid at 20 wt % HCl according to his proposal. This is because there is no possibility of hydrogen chloride absorption into liquors from
30 the second concentrator as proposed. Consequently, the ability to reduce energy consumption via this technique is limited.

In a more complex but more beneficial arrangement for

practising the present invention the preconcentrator and roaster are operated in such a manner as to ensure that crystals of a chloride salt are formed via evaporation of water and absorption of hydrogen chloride. The crystals and
5 the bulk of the associated liquor may then be separated (eg. via settling, cycloning, centrifuging or even filtering.

A mixture of the crystals and a predesignated proportion of the preconcentrator liquors may then be fed to a roaster. In
10 the case of the use of a spray tower roaster it will be advantageous if the crystal/preconcentrator liquor mixture is first redissolved by heating to above the crystallisation temperature of the mixture. The resulting liquor may then be sprayed directly through nozzles without fear of blockage by
15 solid crystals.

The advantage of concentration/absorption to the point of crystallisation lies in the introduction of a stream having much higher chloride to water ratio into the roaster. In
20 this manner the roaster energy consumption is reduced and the hydrogen chloride content of the roaster exit gases is increased. The high hydrogen chloride level in the roaster gases assists in ensuring a sufficient level of absorption in the preconcentrator liquors that the liquors separated from
25 the crystals may be used as a leachant or digestant.

In the improved system it will be advantageous (although not essential) to use a countercurrent gas/liquid contactor as a preconcentrator in order to ensure that liquors recycled to
30 leaching or digestion have an acid strength which is as high as can potentially be achieved.

A preferred embodiment of the invention will now be described with reference to the accompanying drawing which represents

a flow diagram.

Appropriate apparatus for performing the process of the present invention may comprise a leach tank/digester 1, a filter 2, a preconcentrator 3, a crystal separator 4, a crystal redissolver 5, a spray roasting tower 6 and an absorption column 7.

Leachant and mineral or other material which has been prepared for leaching/digestion are fed to the digester 1. Spent leach liquor is withdrawn from the digester 1, passed through the preconcentrator 3 and then into the crystal separation system 4. Crystals and a blend of preconcentrator liquor are fed to the redissolver 5, and the resulting liquor passes to the spray roaster 6. Gases evolved from the spray roaster are passed through the preconcentrator 3 counter current to the flow of leach liquor and then through an absorption column 7 where hydrogen chloride not absorbed into preconcentrator liquor is absorbed in water to produce regenerated hydrochloric acid. In addition, concentrated leach liquor is taken from the preconcentrator 3 and fed into the stream of hydrochloric acid extracted from the bottom of the absorption column 7. The mixture of regenerated hydrochloric acid and concentrated leach liquor is then fed back to the digester 1 as leachant.

Systems for which crystallisation is not pursued will not require the crystal separator or redissolver, and liquor in these cases passes directly from the preconcentrator to the spray roaster after a portion has been removed for recycle to leaching/digestion.

In the case where the disclosed acid regeneration process is applied to the leaching of ilmenite or pretreated ilmenite

for the production of synthetic rutile the spent leach liquor will contain iron chloride, and possibly other chlorides such as magnesium, manganese and aluminium chlorides. In such cases where crystallisation is pursued the crystals will normally be hydrated ferrous chloride crystals, which contain little of the other chlorides. The proportion of the preconcentrator liquor which is fed to the roaster will in this case be determined to ensure a sufficient bleed of other elements to allow their removal without detrimental impact on the process.

Examples: The following examples illustrate the absorption of hydrogen chloride into spent leach liquors in order to allow recirculation of the liquors as leachant.

Example 1: One litre of agitated 45% ferrous chloride solution was held at 95°C, and sparged with a mixture of 2 litres per minute of nitrogen and 1.33 litres per minute of hydrogen chloride (volumes measured at 25°C). After 150 minutes water addition to the resulting crystal slurry was commenced at a rate of 120mL per hour to maintain constant volume. After 2 hours of further sparging the crystal slurry was permitted to settle and a sample of supernatant liquor was taken. Its composition was as follows:

S.G. :	1.43 gcm ⁻³
HCl :	123 gpL
FeCl ₂ :	474 gpL

The gas composition leaving the slurry after two hours was:

HCl :	24% (vol.)
H ₂ O :	40% (vol.)
N ₂ :	36% (vol.)

The supernatant liquor composition represents a very effective leachant, for example for use in leaching of pretreated ilmenite. The hydrogen chloride and water vapour contents of the gas are achievable in roasting of crystal/liquor mixtures for pyrohydrolysis of iron chlorides.

Example 2: A Test was conducted in the same manner as example 1, with the exception that only 0.86 litres per minute of hydrogen chloride was used.

The final liquor composition was:

	S.G. :	1.43 gcm ⁻³
15	HCl :	109 gpl
	FeCl ₂ :	531 gpl

The final gas composition was:

20	HCl :	15.4% (vol.)
	H ₂ O :	48.7% (vol.)
	N ₂ :	35.9% (vol.)

Again, the supernatant liquor will be a very effective leachant and the hydrogen chloride and water vapour contents of the gas are achievable in roasting of crystal/liquor mixtures for pyrohydrolysis of iron chlorides.

The above examples have demonstrated that sufficient acid strengths in liquors exiting a countercurrent preconcentrator can be achieved to render the resulting liquors suitable as leachant, even under conditions of crystallisation, for which hydrogen chloride solubility in liquors is relatively low.

CLAIMS

1. A process for forming an aqueous chloride leachant from a spent aqueous chloride leach liquor which process
5 comprises the steps of:
- a) passing a spent aqueous chloride leach liquor and gases containing hydrogen chloride through a preconcentrator to form a concentrated aqueous
10 chloride leach liquor by partial evaporation of water therefrom and absorption of hydrogen chloride
- b) withdrawing a portion of the concentrated aqueous chloride leach liquor;
15
- c) roasting the remainder of the concentrated aqueous chloride leach liquor to generate a metal oxide and gases containing hydrogen chloride and water vapour therefrom;
20
- d) passing the gases containing hydrogen chloride to step a); and
- e) recovering hydrogen chloride exiting the preconcentrator by dissolving it in water to form
25 regenerated hydrochloric acid.
2. A process according to Claim 1 including the additional step of mixing the regenerated hydrochloric acid with
30 the withdrawn portion of concentrated aqueous chloride leach liquor to form the aqueous chloride leachant.
3. A process according to Claim 1 wherein the spent aqueous chloride leach liquor is passed through the

preconcentrator counter current to the gases containing hydrogen chloride.

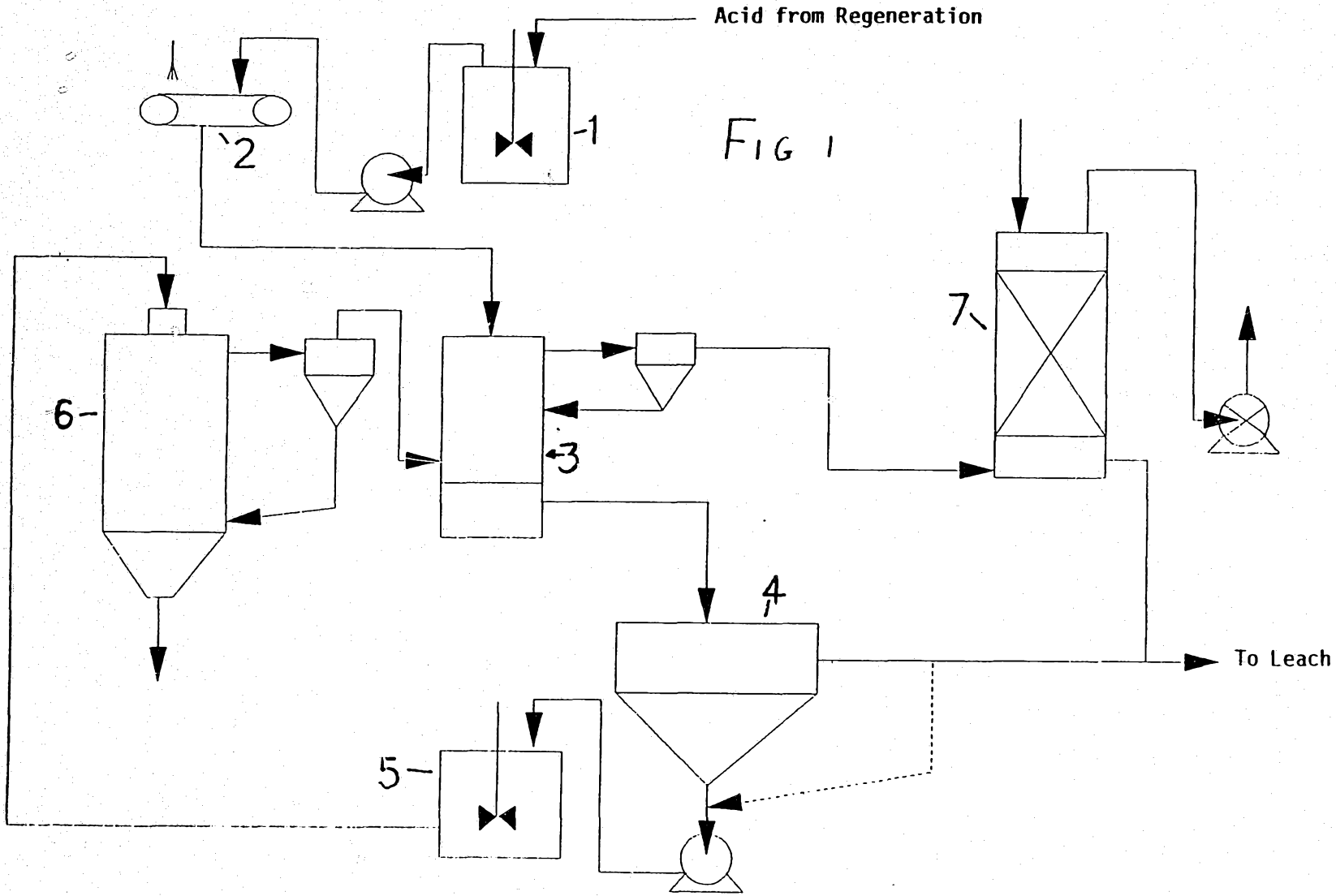
4. A process according to Claim 1 wherein the remainder of the concentrated aqueous chloride leach liquor contains metal chloride crystals.
5. A process according to Claim 4 wherein the process includes the steps of redissolving the crystals to produce a concentrated solution of the metal chloride and spray roasting the concentrated solution of metal chloride.
6. A process according to any one of the preceding claims wherein the spent aqueous chloride leach liquor comprises chlorides of iron and other metals.
7. A process according to any one of the preceding claims wherein the spent aqueous chloride leach liquor is derived from leaching ilmenite or any other titaniferous material.
8. Apparatus for forming an aqueous chloride leachant from a spent aqueous chloride leach liquor, the apparatus comprising preconcentrator means for evaporating water from the spent aqueous chloride leach liquor and contacting it with gases containing hydrogen chloride; extraction means for extracting concentrated aqueous leach liquor from the preconcentrator means and dividing it into first and second portions of concentrated aqueous chloride leach liquor; roasting means for roasting the second portion of concentrated aqueous chloride leach liquor to produce a metal oxide and gases containing hydrogen chloride; absorption

means for absorbing hydrogen chloride in water; first
conduit means for conducting gases generated in the
roasting means to the preconcentrator means; second
conduit means for conducting gases exiting from the
5 preconcentrator means to the absorption means; and
third conduit means for conducting the first portion of
concentrated aqueous chloride leach liquor from the
extraction means the third conduit means having a valve
to control the flow of the first portion of
10 concentrated aqueous chloride leach liquor.

9. Apparatus according to Claim 8 wherein the roasting
means is a spray roaster.
- 15 10. Apparatus according to Claim 8 wherein the second
portion of concentrated aqueous chloride leach liquor
contains crystals of metal chloride.

Acid from Regeneration

FIG 1



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29361/92
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU92/00625

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl.⁵ C01B 7/07, C22B 3/10, 3/02

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)

IPC⁵ C01B 7/07, C22B3/10, 3/02 (IPC⁴ C22B 3/00)

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 practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	AU,B,430122 (57744/69) (NATIONAL LEAD CO.) 14 January 1971 (14.01.71)	1 & 8
A	AU,A,13262/91 (ABB FLAKT AB) 1 March 1992 (01.03.92)	
A	AU,A,26104/77 (TOLEDO PICKLING & STEEL SERVICE INC) 21 December 1978 (21.12.78)	
A	US,A,2677598 (CRUMMETT) 4 May 1954 (04.05.54)	

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