FORM 1
REGULATION 9

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

APPLICATION FOR A STANDARD PATENT

We, RHONE-POULENC CHIMIE, a French Company, of 25, Quai Paul
Doumer, 92408, Courbevoie, Cedex, France, hereby apply for the grant
of a Standard Patent for an invention entitled:-

"PROCESS FOR THE TREATMENT OF ORES CONTAINING RARE EARTHS"

which is described in the accompanying Complete Specification.

Details of basic application:-

Number: 89/11990
Country: France
Date: 13th September, 1989

Our address for service is: SHELSTON WATERS
55 Clarence Street
SYDNEY, N.S.W. 2000.

DATED this 10th Day of September, 1990

RHONE-POULENC CHIMIE

by

Fellow Institute of Patent Attorneys of Australia
of SHELSTON WATERS

To: The Commissioner of Patents
WODEN A.C.T. 2606

File: D.B. R-98
Fee: $325.00
In support of the Convention Application made by...

(a) RHÔNE-POULENC CHIMIE

(hereinafter referred to as "Applicant") for a patent for an invention entitled:
(b) "PROCESS FOR THE TREATMENT OF ORES CONTAINING RARE EARTHS"

1. I am authorised by Applicant to make this declaration on its behalf.
2. The basic Application(s) as defined by section 141 of the Act was/were made
in... France... on the... 13th... day of... September,... 1989
by... RHÔNE-POULENC CHIMIE...
in... France... on the... day of... 19
by... France... on the... day of... 19
by... France... on the... day of... 19
by... France... on the... day of... 19
by...
3. (a) Francine CAILLY of 42 a 52, rue Villiers de l'Isle Adam
75020 - Paris, France and Yves MOTTUT of 14, avenue Salvador
Alliende 93290 - Tremblay En France, France.

The rights to the invention were transferred from the
inventors to the applicant by an agreement signed on
1st September, 1989.

4. The basic Application(s) referred to in paragraph 2 of this Declaration was/were the first
Application(s) made in a Convention country in respect of the invention, the subject of the
Application.

DECLARED at... COURBEVOIE, FRANCE

this... 19TH... day of... SEPTEMBER,... 1990
1. Process for the treatment of ores containing rare earth compounds, characterized in that it comprises

(i) digesting the ore by sulphuric acid

(ii) adding to the digested mass, in the presence of water, a compound comprising a cation which forms an insoluble sulphate and an anion which forms a soluble salt with the rare earths

(iii) separating off and recovering the rare earths after removing the insoluble components.

3. Process according to Claim 1 or 2, characterized in that in step (iii) the precipitation of the rare earths is effected by raising the pH of the solution to a value greater than 6, preferably between 8 and 10.
5. Process according to one of the preceding claims, characterized in that the compound added in step (ii) is an alkaline earth metal nitrate or chloride, such as calcium nitrate or calcium chloride.
Complete Specification for the Invention entitled:

"PROCESS FOR THE TREATMENT OF ORES CONTAINING RARE EARTHS"

The following statement is a full description of this invention, including the best method of performing it known to us:-

- 1 -

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PROCESS FOR THE TREATMENT OF ORES CONTAINING RARE EARTHS

The present invention relates to a process for the treatment of an ore containing rare earths. At present, the main rare earth ores to be exploited are those containing minerals carrying rare earths, such as monazite, bastnasite and xenotime. There exist a large number of other ores, the exploitation and treatment of which are currently not profitable.

In the case where the ore has a low or medium content of rare earth elements, it is necessary to concentrate it by subjecting it to a physical treatment: gravimetry, flotation or magnetic separation. Such a process, which is in addition to the chemical treatment necessary for the recovery of the rare earth elements, can prove costly and make the process uneconomical.

One of the objects of the present invention is to provide an economical process for the recovery of rare earths from the ore containing them by means of a process which makes it possible, in particular, to avoid or limit prior concentration of the said ore.

Another object of the present invention is to have available a process suitable for the treatment of any type of ore or residue containing rare earth elements, irrespective of their concentration.

The object of the invention is also to
provide a process suited more specifically to the
treatment of ores comprising fluorinated compounds of
rare earths, such as the bastnasite ores, which contain
fluorocarbonates of rare earths, thus making it
possible to eliminate fluorine without the need for
heat treatments at high temperature.

To this effect, the invention proposes a
process for the treatment of ores containing rare earth
compounds which comprises the following steps:

(i) digestion of the ore by sulphuric acid
(ii) addition to the digested mixture, in the
presence of water, of a compound comprising a cation
which forms an insoluble compound with the sulphate
anion and an anion which forms a soluble compound with
the rare earths;
(iii) recovery of the rare earths after removing of
the insoluble components.

According to a characteristic feature of the
invention, the separation and recovery of the rare
earths are effected by adding a compound forming an
insoluble compound with them.

Thus, solubilizing the rare earths by
exchanging the sulphate anion for another anion, such
as, for example, nitrate, halide, acetate or
perchlorate anions, makes it possible to prevent the
formation of the sulphate double salt, which is
difficult to dissolve, and to achieve an almost
complete recovery of the rare earths.
According to another characteristic feature of the invention, the compound added in step (ii) is advantageously a nitrate or a chloride, such as an alkaline earth metal nitrate or chloride or the like.

The preferred compound of the invention, especially from an economic point of view, is calcium nitrate or calcium chloride.

The compound is used in an amount sufficient to obtain complete dissolution of the rare earths or, more simply, almost complete precipitation of the sulphate anions present. Thus, the ratio of the cation of the compound to the sulphate anion must be at least equal to the stoichiometry, advantageously 10 % more than that, and preferably has an excess of the cation of the salt equal to about 50 % of the stoichiometry.

The solution of rare earths is separated from the insoluble components by any conventional solid/liquid separation process, such as, for example decanting, filtration, centrifugation or the like.

The rare earths are then recovered by precipitation in the form of an insoluble compound, in general in the form of hydroxides or carbonates. This precipitation is effected by increasing the pH of the solution by adding a basic compound, such as a soluble carbonate or hydroxide.

According to a preferred embodiment of the invention, this precipitation is effected by adding a carbonate or hydroxide comprising at least the cation.
of the compound added in step (ii), in order to regenerate it and recycle it into this step (ii). Thus, in the case where the compound is calcium nitrate, it is advantageous to use lime as basic compound for raising the pH of the solution.

This feature represents an important advantage from an economical point of view and with respect to the effluent discharge. Indeed, the recycling of the solution obtained after the precipitation of the rare earths in step (ii) makes it possible to diminish or even eliminate the liquid effluents and especially the discharge of nitrate compounds. Thus, in the case where lime and calcium nitrate are used, the discharges essentially consist of calcium sulphate and the reactants consumed are essentially lime and sulphuric acid.

In the case where the rare earths are precipitated in the form of hydroxides, the pH of the solution is raised to a value greater than 6 and advantageously between 8 and 10.

According to another feature of the invention, it is advantageous to raise the pH of the solution in two steps, a first step during which the pH is raised to a value below 5.5, advantageously below 4.5, to precipitate the elements other than the rare earths, such as iron, aluminium or the like.

This step of raising the pH of the solution to a value below 5.5 is carried out either before the
removal of the insoluble components or after this removal. In the latter embodiment, an additional step, in which the insoluble compounds are separated, has to be carried out before precipitating the rare earths.

Moreover, when this step of precipitating the impurities is not carried out, their removal can be achieved by converting the final concentrate into a pulp. This very expensive step makes the process significantly less economical.

Furthermore, the process of the invention can be adapted by choosing the salt anion added in step (ii) as a function of the major impurities accompanying the rare earth elements.

Thus, if the ore does not contain manganese or does so in only very small amounts, it is more advantageous to use a chloride, such as, for example, calcium chloride, in step (ii). Indeed, calcium chloride is more economical and less of a hazard with respect to the environment.

After removal of the undissolved substances, the pH of the solution is raised to a value greater than 6, in order to precipitate the rare earth elements.

The rare earth precipitate obtained can then be treated to separate the rare earths from one another or to separate mixtures of rare earths by means of processes well known to those skilled in the art.

Thus, the rare earth precipitate obtained
after step (iv) is a raw material for the processes for separating rare earths, which are known and in use.

By way of example, this precipitate can be taken up in an acid, such as hydrochloric or nitric acid, for example to obtain a concentrated solution of rare earth salts. The rare earths can then be separated by means of a conventional liquid/liquid extraction process.

Another advantage of the invention lies in the fact that the process makes it possible to treat any type of ore or residue containing rare earths.

The process of the invention can be applied to any type of ore and more specifically to ores having a low rare earth content.

It is obvious that it is not beyond the scope of the present invention if the process is carried out with ore concentrates, the preparation process of which is well known, for example by concentration with the aid of physical techniques, grinding and flotation and/or concentration by gravity on vibrating tables and/or by magnetic separation and/or any other physical or chemical technique.

It is likewise possible to use an ore which has been subjected to a heat pretreatment.

In the case of low-grade rare earth ores, an ore having a gangue which is partially insoluble in sulphuric acid is preferably used, it being possible for quartz and silicates, magnetite, anatase, rutile,
ilmenite, garnets and zircons to be mentioned.

Examples of ores suitable for implementing the invention are ores whose rare earth-carrying constituents are phosphates, fluorocarbonates, carbonates or silicates.

By way of example, the following ores whose average rare earth content by weight, expressed as rare earth oxides, is detailed below can be mentioned:

- ores of the phosphate type, such as apatites, where the rare earths are incorporated in the calcium phosphate lattice $\text{Ca}_5(\text{PO}_4)_3(\text{F}, \text{Cl}, \text{OH})$ (10 %); rhabdophanite $\text{REPO}_4$, $\text{H}_2\text{O}$ (60 %); monazite $\text{REPO}_4$ (65 %).
  Churchite $\text{REPO}_4$, $\text{H}_2\text{O}$ (50 %); the group of crandallites, for example florencite $\text{REAl}_3(\text{PO}_4)_2(\text{OH})_6$ (30 %);

- ores of the fluorocarbonate type, for example bastnasite $\text{RECO}_3\text{F}$ (75 %), synchisite $\text{RECa}(\text{CO}_3)_2\text{F}$ (52 %);

- ores of the carbonate type, especially lanthanite $\text{RE}_2(\text{CO}_3)_3$, $\text{8H}_2\text{O}$ (55 %);

- ores of the silicate type, especially allanite $(\text{RECa})_2(\text{FeAlMg})_3(\text{SiO}_4)(\text{Si}_2\text{O}_7)\text{O(OH)}$ (25 %), britholite $\text{RE}_2\text{Ca}_2(\text{SiO}_4)_3\text{OH}$ (60 %), eudialite $(\text{Na,Ca})_5(\text{Zn,Fe,Mn})\text{Si}_5\text{O}_{17}(\text{O,OH,Cl})$.

The process of the invention is entirely suitable for the treatment of ores of the fluorocarbonate type.
Indeed, the fluorine content in the ore is released, as a result of the sulphuric acid digestion, especially in the form of hydrofluoric acid.

It is likewise possible to treat, according to the process of the invention, any type of residue whether in solid or liquid form.

Thus, it is possible to use residues containing rare earths in salt form (phosphates, carbonates or sulphates) or residues (powders, turnings, fragments, bars, dusts, etc.) which usually result from the manufacture of magnets of the RE/Co type, where the rare earth is essentially samarium, or RE/Fe/B, where the rare earth is essentially neodymium, and where the atomic percentage of the elements is in general as follows: 8 to 30 % of rare earth; 2 to 28 % of boron, and the balance iron.

The process is likewise suitable for the treatment of residues from the dissolution of gypsum, especially of gypsums resulting from sulphuric acid digestion of phosphate ores, and the slurries obtained from the concentration or desaturation step of crude phosphoric acids.

It is likewise possible to treat, according to the process of the invention, the waste from iron mining, which still contains iron oxides and apatite. In a similar manner, before the process of the invention is carried out, it is desirable to remove the magnetite by magnetic separation, a technique which is
well known in the field in question.

The list of ores and residues cited above is in no case limiting. In the following description of the invention, "ore" is understood to mean not only an ore but also a residue containing rare earths.

In accordance with the process of the invention, digestion of the ore with the aid of sulphuric acid is carried out in step (i), for example by converting the ore into a paste or pulp.

Before the acid digestion, a crushing and/or grinding operation may prove advantageous, in order to release the mineral component carrying the rare earths. The particle size depends on the mesh used, which can vary between a few microns, in general 4 to 5 μm, and 2 mm. However, if a fairly rapid digestion is desired, it is advantageous to use particles having a diameter of less than 1 mm.

The crushing and grinding operations can be carried out by conventional methods, for example in a jaw crusher and/or a ball or rod mill mounted in an open or closed or classifying circuit.

Apart from the minerals carrying the rare earths, certain mineral impurities are likewise digested by the sulphuric acid. However, these impurities can be removed in the course of the process or in a later step.

The digestion of the ore is effected by sulphuric acid. The concentration of the sulphuric acid
is not critical for this. Thus, it is possible to use an oleum as sulphuric acid solution. In the latter case, the concentration of the sulphuric acid solutions is advantageously between 45 % and 100 % by weight, preferably between 75 % and 95 %.

The amount of sulphuric acid used is a function of the amount of materials which can be digested by sulphuric acid (rare earths and impurities). This amount is preferably equal to the stoichiometric amount required for digesting the digestible elements.

Advantageously, this quantity may be greater than the stoichiometric amount required, this excess being preferably of the order of 20 %, advantageously between 5 and 10 %.

In order to improve the yield of the acid digestion and especially the kinetics of this digestion, it is advantageously carried out at a temperature greater than 100°C, in order to remove the water present and thus shift the equilibrium. The digestion may be carried out at a temperature between 100°C and about 400°C.

Other advantages, details and objects of the invention will become more clearly apparent from the examples given below by way of guidance and the detailed description of a preferred embodiment of the invention, which is given with reference to the single attached figure representing a block diagram of a
preferred embodiment of the invention.

The process of the invention in one preferred embodiment comprises converting a rare earth ore in a reactor 1 to a sulphuric acid paste by adding a solution of sulphuric acid at 2.

After the reaction and digestion by sulphuric acid, a solution of a salt comprising a cation forming an insoluble sulphate and an anion forming a soluble salt with the rare earths, for example a calcium nitrate solution, is added in a reactor 3. This addition takes place at 4.

Thus, the rare earth elements are dissolved in the reactor 3. The reaction mixture thus obtained is introduced into a reactor 5. The pH of this medium is then raised to a value below 5.5, for example 3, by adding lime at 6.

Thus, the impurities such as iron and aluminium, which went into solution when the calcium nitrate solution was taken up at 3, precipitate, in general in the form of a hydroxide.

The reaction medium is then filtered at 7 and the insoluble components which are made up especially by the materials which were not digested by the sulphuric acid and the impurities precipitated in the reactor 5, are removed at 8.

The liquid phase is then fed at 9 into a new reactor 10. In this reactor 10, the pH of the liquid phase is raised to a value greater than 6, for example
8.5, by adding lime at 11, in order to achieve in this manner precipitation of the rare earth elements in the form of a hydroxide.

Likewise, calcium carbonate can be used to raise the pH, in which case the rare earths are then precipitated in the form of a carbonate.

The rare earth precipitate is separated at 12 and recovered at 13. The liquid phase containing mainly calcium nitrate is then recycled at 4 into the reactor 3.

It will be appreciated that the circuit in which the calcium nitrate solution is recycled can comprise a purge 4a and an inlet 4b for feeding fresh solution, so as to adjust and control the calcium nitrate content of the solution and its throughput.

The recycling loop 4 of the calcium nitrate solution is not absolutely necessary for the process. Indeed, it is easily conceivable that the solution added in the reactor 3 can be a fresh solution of a salt and the liquid phase separated at 12 can be removed as effluent. This embodiment is especially used in the case where the cation of the compound added at 4 to the reactor 3 differs from the cation of the compound used for raising the pH in the reactors 5 and 10.

However, the embodiment illustrated is preferred because the recycling of the liquid phase makes it possible to reduce the amount of effluents.
discharged.

It is likewise easily understandable that the liquid phase collected at 12 can be recycled completely or partially.

Furthermore, depending on the type of impurities accompanying the rare earths, the raising of the pH carried out in the reactor 5 can be dispensed with, the rare earths in this case being precipitated directly at 10 without prior elimination of impurities.

Exemplary embodiments of the invention are given below to illustrate the invention, without limiting it, however. The percentages given are by weight, unless stated otherwise.

Example 1

100 g of ore having an average particle size below 100 µm and a rare earth content (expressed as oxide, RE₂O₃) of 28% and containing fluorine, phosphorus and a large number of other elements are digested by 120 g of 92% strength sulphuric acid at 300°C for two hours.

The mixture thus obtained is broken up into small pieces and then subjected to leaching with two litres of a 100 g/l calcium nitrate solution.

This leaching is carried out at ambient temperature (of the order of 20°C) for 1 hour.

The mixture obtained in the form of a pulp is then treated with lime milk containing 200 g/l of CaO, to give a mixture with a pH of 3.
The reaction mixture is then filtered and washed with water.

The solution obtained contains 13.1 g/l of rare earths expressed as RE₂O₃.

This solution is heated to 80°C, and lime milk containing 200 g/l of CaO is added until the pH has risen to 8.5. The rare earths precipitate in the form of hydroxides and are recovered by filtration, washing with water and drying at 120°C.

The process allows the recovery of 33.2 g of a rare earth precipitate of the following composition:

- rare earths (expressed as RE₂O₃) : 82.1 %
- calcium (expressed as CaO) : 0.8 %
- loss on heating to 900°C : 13.1 %
- others : 4.0 %

**Example 2**

Example 1 is repeated, except that the leaching of the digested mass is carried out using a 90 g/l calcium chloride solution.

Under these conditions, the process allows the recovery of 33.5 g of precipitate having the following composition:

- rare earths (expressed as RE₂O₃) : 81.2 %
- calcium (expressed as CaO) : 1.0 %
- loss on heating to 900°C : 14.0 %
- others : 3.8 %

**Example 3**

100 g of ore having an average particle size
of less than or equal to 100 μm and containing 32.8 % of rare earths expressed as oxide, fluorine and a large number of other elements are digested by 100 g of 62 % strength H₂SO₄ at 200°C for 2 hours.

After the digested mass has been broken up into small pieces, it is subjected to leaching with 1 litre of a 200 g/l calcium nitrate solution at ambient temperature for 1 hour.

The pulp obtained is treated with a 200 g/l lime milk, to raise the pH to a value equal to about 3.5.

After filtration, the solution obtained contains 30 g/l of rare earths expressed as RE₂O₃.

The rare earths are precipitated by adding a 200 g/l lime milk, during which a pH of about 8.5 is obtained.

After filtration, washing and drying, the rare earth precipitate has the following composition:

- rare earths (RE₂O₃) : 73.8 %
- calcium (CaO) : 0.9 %
- loss on heating to 900°C : 16.4 %
- others : 8.9 %

These rare earth precipitates can then be taken up by an acid, for example nitric acid, in order to be used as raw materials in the processes for separating rare earths, such as the liquid/liquid extraction processes.
THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. Process for the treatment of ores containing rare earth compounds, characterized in that it comprises
   (i) digesting the ore by sulphuric acid
   (ii) adding to the digested mass, in the presence of water, a compound comprising a cation which forms an insoluble sulphate and an anion which forms a soluble salt with the rare earths
   (iii) separating off and recovering the rare earths after removing the insoluble components.

2. Process according to Claim 1, characterized in that the recovery of the rare earths is effected by precipitation by adding a compound forming an insoluble compound with the rare earths.

3. Process according to Claim 1 or 2, characterized in that in step (iii) the precipitation of the rare earths is effected by raising the pH of the solution to a value greater than 6, preferably between 8 and 10.

4. Process according to Claim 1 or 2 or 3, characterized in that the compound added in step (ii) is a nitrate or a chloride.

5. Process according to one of the preceding claims, characterized in that the compound added in step (ii) is an alkaline earth metal nitrate or chloride, such as calcium nitrate or calcium chloride.
6. Process according to one of the preceding claims, characterized in that the pH is increased by adding a hydroxide or a carbonate.

7. Process according to one of the preceding claims, characterized in that prior to step (iii) the pH of the solution from step (ii) is raised to a pH below 5.5, preferably below 4.5.

8. Process according to one of the preceding claims, characterized in that the insoluble components are removed after step (ii).

9. Process according to one of the preceding claims, characterized in that the ore is an ore whose rare earth-carrying compounds are phosphates, fluorocarbonates, carbonates or silicates or any residue containing rare earths in salt or metal form.

10. Process according to one of the preceding claims, characterized in that the ore used is an ore containing apatite or an ore containing bastnasite.

11. Process according to one of the preceding claims, characterized in that the ore used is a residue from the manufacture of magnets of the samarium/cobalt or neodymium/iron/boron type.

12. Process according to one of the preceding claims, characterized in that the ore used is a residue from the dissolution of gypsum resulting from the sulphuric acid digestion of phosphate ores or the slurries obtained from the concentration step of crude phosphoric acids.
13. Process according to one of the preceding claims, characterized in that the digestion of the ore is effected by converting the ore into a paste by means of sulphuric acid.

14. Process according to one of Claims 1 to 12, characterized in that the digestion of the ore is effected by converting the ore into a pulp by means of sulphuric acid.

15. Process according to one of the preceding claims, characterized in that the hydroxide or carbonate added to raise the pH in step (iii) and/or prior to step (iii) comprises a cation of the same type as that of the salt added in step (ii).

16. Process according to Claim 15, characterized in that the liquid phase obtained after step (iv) is recycled into step (ii).

17. Process according to one of the preceding claims, characterized in that the amount of the compound added in step (ii) is sufficient to result in a ratio of the cation of the compound to the sulphate anion present in the leached mass which is at least equal to that of the stoichiometry, preferably 10 % greater than that.

18. Process according to Claim 17, characterized in that the ratio of the cation of the compound to the sulphate anion is 50 % greater than the stoichiometric ratio.

19. Process according to one of the preceding
claims, characterized in that the digestion step (i) is carried out at a temperature between 100°C and 400°C.

20. Process according to one of the preceding claims, characterized in that the sulphuric acid used for step (i) is a sulphuric acid solution of a concentration between 45 % and 100 %, preferably between 75 % and 95 %.

21. Process according to one of Claims 1 to 19, characterized in that the sulphuric acid used in the digestion step (i) is oleum.

22. Process according to one of the preceding claims, characterized in that the amount of sulphuric acid used in step (i) is at least equal to the theoretical amount required to digest the digestible elements of the ore.

23. Process according to Claim 22, characterized in that the abovementioned amount of sulphuric acid is 20 % greater than the theoretical amount, this excess preferably being between 5 and 10 % of the theoretical amount.

24. A process for the treatment of ores containing rare earth compounds substantially as herein described with reference to any one of the examples.

DATED this 10th Day of September, 1990

RHONE-POULENC CHIMIE

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Fellow Institute of Patent Attorneys of Australia
of SHELTON WATERS