MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS—1963 A
We, RHONE-POULENC CHIMIE, of 25, Quai Paul Doumer, 92408, COURBEVOIE, FRANCE, hereby apply for the grant of a Standard Patent for an invention entitled:—

"METHOD FOR THE SEPARATION OF RARE EARTHS"

which is described in the accompanying Complete Specification.

Details of basic application:—

Number: 36/03889
Country: FRANCE
Date: 19th March, 1986

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SYDNEY, N.S.W. 2000.

DATED this 18th day of March, 1987

RHONE-POULENC CHIMIE

by

Ilow Institute of Patent Attorneys of Australia
of SHELSTON WATERS

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

File: D.B.19G
Fee: $260.00
COMMONWEALTH OF AUSTRALIA PATENTS ACT, 1952-1973

DECLARATION IN SUPPORT OF A CONVENTION APPLICATION FOR A PATENT

In support of the Convention Application No. (a) made by (b) in support of the Basic Application(s) by (c) in support of the Basic Application(s) made in (d) by (e) and (f) (g).

(a) Here Insert (in full) Name of Company.

(b) Here Insert Title of Invention.

(c) Marie-Claude DUTRUC-ROSSET

(d) RHONE-POULENC INTERSERVICES

25, quai Paul Doumer 92408 COURBEVOIE CEDEX, FRANCE

do solemnly and sincerely declare as follows:

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 on the (h) day of (i) March, 19( (j) 86

3. ALAIN LEVEQUE, of 18, rue du General Guillaumat-17000-LA ROCHELLE, FRANCE and JEAN-LUC LE LOAER, of 24, rue du General Guillaumat-17000-LA ROCHELLE, FRANCE

are the actual Inventor(s) of the invention and the facts upon which Applicant is entitled to make the Application are as follows:

Applicant is the Assignee of the said Inventors, RHONE-POULENC CHIMIE DE BASE who is the Assignee of the said Inventors.

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 this (k) day of (l) May, 19( (m) 87

(h) Marie-Claude DUTRUC-ROSSET

(Signature of Declarant)

To THE COMMISSIONER OF PATENTS.

SHELSTON WATERS
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Cables: Valid Sydney Telex: 24422
1. A method for the separation of neodymium or didymium from rare earths contained in bastnasite, characterised by the steps of:

- calcination of the bastnasite,
- lixiviation of the calcined bastnasite with a nitric acid solution so as to dissolve the neodymium and the trivalent rare earths but not any cerium and traces of thorium which are present in the form of an insoluble residue,
- separation and purification of the neodymium or didymium by liquid-liquid extraction between the aqueous phase composed of the aqueous solution of rare earth nitrates recovered at the previous stage and an organic phase containing an extraction agent, insoluble in water, then recovering the neodymium or didymium from the organic phase.
The following statement is a full description of this invention, including the best method of performing it known to me/us:-

- 1 -
METHOD FOR THE SEPARATION OF RARE EARTHS

This invention relates to a process for the separation of rare earths found in ores or rare earth concentrates rich in fluocarbonates, notably bastnasite. It deals more precisely with a perfected process for the separation of neodymium, if necessary in association with praseodyme from other rare earths contained in bastnasite.

The term "rare earth" used in relation to the invention includes the rare earth elements with atomic numbers from 57 to 71 inclusive and yttrium with the atomic number 39.

In the explanation of the invention which follows, by "ceric rare earths", we mean the lighter elements of rare earths starting with lanthanum and proceeding to neodymium in accordance with the atomic number, and by "yttric rare earths", we mean the heavier elements of rare earths in accordance with the atomic number, starting with samarium and ending with luteceum and including yttrium. "Trivalent rare earths" are the elements of rare earths with the atomic numbers 39, 57, 59 to 71.

The term "didymium" is the usual name given to a mixture of neodymium and praseodymium in whatever proportions.

The term "bastnasite" is used to denote, in the wider sense a rare earth ore which includes rare earth fluocarbonates with or without other constituents, particularly mineral gangue as well as concentrates of these ores.

The development of magnets from rare-earths and particularly those with a neodymium or praseodymium base alloyed with iron necessitates the use of methods of separation which perform well technically and are also financially viable.

The methods used at present to obtain rare earths from ores are directed either toward the valorization of the whole of the rare earths obtained, which is unwieldy and costly, or towards valorizing a fraction of the ore, rich in rare earths and fetching high prices, particularly europium, yttric rare earths and yttrium.
Numerous processes have been described and are applied in the industry to achieve these aims, using the usual raw materials such as monazite, bastnasite or xenotime.

The processes suggested for the complete valorization of the rare earths are generally those where they are attacked with soda and the hydroxides obtained are redissolved in hydrochloric or nitric acid. For solutions of rare earth chlorides or nitrates, the rare earths are separated from one another by successive liquid-liquid extractions.

In the case of bastnasite, the ore can be pre-calcined as described in Deco Trefoil, November-December 1967, P.9, this allows during the recovery with hydrochloric acid for only a portion of the cerium to be dissolved with the mixture of other rare earths. Using a solution of rare earth chlorides, the europium and a fraction of the yttric rare earths are separated by a solvent.

As mentioned previously, although these methods allow the neodymium and praseodymium to be recovered, they do not give the required economic results in relation to the aims.

The objective of this invention is a thoroughly efficient and viable method for the separation of neodymium didymium contained in bastnasite.

The invention consists in a method for the separation of neodymium or didymium from rare earths contained in bastnasite, characterised by the steps of:

- calcination of the bastnasite,
lixiviation of the calcined bastnasite with a nitric acid solution so as to dissolve the neodymium and the trivalent rare earths but not any cerium and traces of thorium which are present in the form of an insoluble residue,

- separation and purification of the neodymium or didymium by liquid-liquid extraction between the aqueous phase composed of the aqueous solution of rare earth nitrates recovered at the previous stage and an organic phase containing an extraction agent, insoluble in water, then recovering the neodymium or didymium from the organic phase.
With this invention it is to be noted that an excellent selectivity of cerium/other rare earths is obtained with the selective lixiviation with a nitric acid solution. It is also evident that the thorium reacts in a similar manner to cerium during lixiviation so that the method of this invention has the advantage of simultaneously eliminating the cerium and the traces of thorium found in bastnasite.

However, small quantities of cerium and thorium may dissolve in the nitric acid solution. In this invention, the dissolved cerium is in a tetravalent state which allows it to be easily and simultaneously separated from the thorium of the mixture of trivalent rare earths, for example by pre-neutralising when small quantities of cerium and thorium in the form of a solid residue are eliminated, this residue also contains small amounts of fluorine dissolved at the time of the nitric recovery.

The careful lixiviation of the bastnasite with a solution of nitric acid allows the selective dissolution of the trivalent rare earths excluding the cerium, the soluble traces of which are principally, in tetravalent form. Selective lixiviation such as this is known and described using hydrochloric acid in FR 1 503 042 for example, but there, the cerium is dissolved to a trivalent state and is therefore difficult to separate from the other trivalent rare earths.

Furthermore, the fact of using a nitric medium widens the choice of extraction solvents which are then used for the separation of the rare earths from one another. Anionic, cationic and solvating extraction agents can then be used which is not the case in a hydrochloric medium which usually only allows the separation of rare earths with cationic extraction agents.

According to the invention, bastnasite is the source of rare earths being essentially a rare earth fluocarbonate.

The rare earths present are ceric rare earths, lanthanum, cerium, praseodymium and neodymium and other rare earths known as yttric may represent up to approximately 3%, more often 2% of the total weight of oxides. Thorium may also be present in a quantity which is at most 1.5% of the total oxides but more often as traces only, representing less than 0.5% of the weight.
According to the invention, it is preferable to use a bastnasite ore containing more than 10% by weight of rare earths as rare earth oxides.

It is better however to use bastnasite ore concentrates obtained in the usual way by enrichment obtained by mechanical means, crushing, flotation or gravity concentration on a jigging table and/or enrichment by chemical means, e.g. processing with an acid, notably a diluted solution of hydrochloric or nitric acid with a concentration of about 10%, in order to eliminate the calcite.

The bastnasite concentrates usually have a rare earth content in oxides which vary from 40 to 75%.

The first stage of the invention involves the calcination of the bastnasite at a sufficiently high temperature to transform the trivalent rare earths into a form which can be dissolved at the following stage of lixiviation with nitric acid and transform the cerium into a form which renders it less soluble.

The calcination is done at a high temperature which should be higher than 400°C. Beyond this, the temperature is not critical but for efficiency and a reasonable duration for the operation a temperature of 600 to 800°C is preferable.

The duration of the calcination depends on the temperature at which it is done; the higher the temperature, the shorter the time. The calcination usually takes between 30 minutes and 3 hours.

After calcination the bastnasite is lixiviated in an aqueous solution of nitric acid which selectively dissolves the trivalent rare earths.

The concentration of the nitric acid solution is not critical; it may vary widely, for example from 1 to 14 N but for preference an aqueous solution of nitric acid with a 3 to 9 N concentration is used.

The quantity of acid used is important in this process; it is determined in relation to the efficiency of dissolution and of the selectivity which is sought for the separation of the cerium from the other rare earths. An excellent separation cerium/rare earths allied to a very good level of recovery of
trivalent rare earths, in particular neodymium is obtained by using a quantity of acid which corresponds to the stoechiometry of the trivalent rare earths. This quantity may of course be variable according to the origin of the bastnasite which may cause a variation in the distribution of the rare earths; more often the bastnasites contain approximately as much cerium as other rare earths and this being the case, the quantity of acid used corresponds to half the stoechiometry of all the rare earths, including the cerium in the original ore. The amount of acid used for preference is the quantity which is approximate to the stoechiometry of the trivalent rare earths but it is possible to use as much as 50% of the stoechimetric quantity.

The lixiviation is done at a temperature which is not determinant and which may be selected between 20 and 90°C.

The length of time during which it remains in the lixiviating solution depends up to a point on the ore and the conditions of the calcination. Its duration is usually between 30 minutes and 2 hours.

Good separation is obtained when processed at 60°C for a duration of one hour.

After this, the aqueous solution of rare earth nitrates is separated from a solid residue using the usual liquid-liquid separation method, e.g. filtration or centrifugation.

A solid residue is obtained containing cerium, principally in the form of an oxide as well as possibly traces of thorium. This residue can be valorized as it is a cerium concentrate.

Concerning the lixiviation solution which is recovered, we would indicate that when the process is carried out in the given preferred manner, less than 10% of the cerium and more than 90% of the trivalent rare earths are dissolved in it including the neodymium originally present in the bastnasite.

The concentration of rare earths in the solution obtained depends on the concentration of nitric acid used for the lixiviation. Under the conditions preferred, the concentration expressed as rare earth oxides is between 150 and 500 g/l.

For further separations it may be useful to eliminate
the traces of tetravalent cerium and thorium which are present in the aqueous solution of rare earth nitrates.

For this purpose the solution is pre-neutralised with a base which is preferably ammonium hydroxide or soda.

The quantity of base added, in solid form, gaseous in the case of ammonium hydroxide or as an aqueous solution is determined so that the pH of the aqueous solution of rare earth nitrates is between 2 and 4.

Under these pH conditions the tetravalent cerium is precipitated, also the thorium and fluorine dissolved during the nitric recovery.

The precipitate is separated in the usual way and an aqueous solution of rare earth nitrates is recovered from which the neodymium or the didymium is recovered.

The separation of the neodymium or the didymium from the other trivalent rare earths is done by liquid-liquid extraction between an aqueous phase containing the rare earth nitrates and an organic phase containing an extraction agent non soluble in water then a counter-extraction of the neodymium and didymium from the organic phase.

The extraction agent used in the method according to the invention can be selected from all the extraction agents having selectivity between the rare earths.

The extraction agent used may be selected from the class of anionic extraction agents, solvating extraction agents or cationic extraction agents.

The anionic extraction agents used are long chain organic compounds with amine functions. The hydrocarbonated chains of these compounds, generally, for preference having between 5 and 30 carbon atoms.

The following are examples of these:

- tertiary amines, in particular products marketed under the name of Alamine 336 and Adogen 364 which are made up of tertiary amines with the formula $R_3N$ where the hydrocarbonated radical $R$ has from 8 to 10 carbon atoms.
- the quarternary ammonium nitrates, particularly the products derived from those marketed under the name of Adogen 464 and
Aliquat 336 which are composed of quartenary ammonium salts with the formula:
\[ \left[ R_3N - CH_3 \right]^+ Cl^- \]
in which the hydrocarbonated radical has from 8 to 10 carbon atoms.

The cationic extraction agents used are the organo-phosphuretted acids, aliphatic or aromatic acids, halogenated or not: napthenic acids β-diketones.

From these, we cite:
- organo-phosphuretted acids with the general formula:
  \[
  \begin{align*}
  &OR_1 \quad OR_1 \quad R_1 \\
  &R_2O - P = O \quad R_2 - P = O \quad R_2 - P = O \\
  &OH \quad OR \quad OH
  \end{align*}
  \]
in which \( R_1 \) and \( R_2 \) represent hydrocarbonated aliphatic or aromatic radicals such that the total number of carbon atoms of these groupings is at least 10. We prefer to use di(ethyl-2 hexyl) phosphoric acid and bi(ethyl-2 hexyl) phosphonic acid:
- commercialised carbosylic acids sold by the Shell Company under the name of "VERSATIC" which have the following general formula:
  \[
  \begin{align*}
  &R_1 \quad CH_3 \\
  &R_2 \quad OH
  \end{align*}
  \]
in which \( R_1 \) and \( R_2 \) are hydrocarbonated radicals either substituted or not and in particular "Versatic 10" acid (registered trade mark derived from the Shell process of carboxylation of olefines to C9 and in which \( R_1 \) and \( R_2 \) are hydrocarbonated radicals, the sum of the carbon atoms of the two radicals being 7:

The solvating extraction agents used are, in particular, the sulfoxides, the neutral organosphosphuretted compounds.

Among these:
- the sulfoxides with the common formula:
in which \( R_1 \) and \( R_2 \) are aromatic and/or aliphatic hydrocarbonated radicals with for preference at least 4 carbon atoms and, for example, di-n-heptylsulphoxide, di-n-octylsulphoxide;
- neutral organo-phosphuretted compounds with the common formula:

\[
\begin{align*}
R_1 & \quad \text{OR} \quad R_2 \quad \text{OR} \\
R_3 \quad \text{OR}_3 & \quad \text{OR}_3 \\
R_1 \quad \text{OR} & \quad R_2 \quad \text{OR} \\
R_3 & \quad R_3
\end{align*}
\]

in which \( R_1, R_2 \) and \( R_3 \) represent hydrocarbonated aromatic or cycloaliphatic radicals and/or aliphatics with preferably at least 4 carbon atoms.

For example, tributylsulphate, dibutyl butylphosphonate, bi (ethyl-2 hexyl) ethyl-2 hexyl phosphonate, tri-n-octylphosphine oxide.

Of these compounds, tributyl phosphate is the one which is preferred.

The organic phase in accordance with the invention may contain, as well as the extraction agent, an organic diluent.

The diluents to be used are those normally employed for liquid-liquid extractions. For example, aliphatic hydrocarbons, dodecane and petroleum by products of the kerosene type; aromatic hydrocarbons such as petroleum by-products composed of a mixture of alkylbenzenes particularly products of the Solvesso type marketed by EXXON.

Amixture of these diluents may also be used.

The proportion of extraction agent used in the organic phase is not critical and may vary widely. It is however advisable for this to be as high as possible. If anionic or cationic extraction agents are used, a proportion between 10 and 40\% by volume in relation to the organic phase give hydrodynamic conditions of separation which are satisfactory. If solvating
extraction solvents are used, some of them (the less viscous) may be used neat, i.e. non diluted, which is extremely useful, as this produces a high capacity of extraction.

The organic phase, in accordance with the invention may also contain various modifying agents one of the essential aims of which is to improve the hydrodynamic properties of the system without altering the complex properties of the extracting agent. Among the suitable compounds are the compounds having an alcohol function and in particular the heavy alcohols having a number of carbon atoms from 4 to 15. A proportion up to 20 % by volume in relation to the organic phase is usually satisfactory.

The separation of the individual trivalent earths is carried out counter-current over several theoretical stages of extraction, each state consisting of a mixing-decanting operation.

The aqueous solution of rare earth nitrates to be separated is introduced at an intermediate stage of the system, at counter-current thereby creating two zones of separation "extraction" and "selective leaching" on either side of this feed point. At each end of this device a partial back flow of the solutions containing the separated elements is created by using the processes which are adapted to the properties of the extraction agents used, acid or base for a cationic extraction agent, water or vapour to dilute or concentrate in the case of or anionic extractants. The efficiency of the separation depends on the number of stages and the separation factor.


After the extraction and leaching process followed by the separation of the aqueous phase from the organic phase, a counter-extraction of the rare earths in the extracting solvent is carried out.

The, or the several rare earths extracted in the organic phase are separated by placing this phase in contact with water or a slightly acid solution, roughly less than 1 N, preferably
a solution of nitric acid, for anionic or solvating extraction agents or a more concentrated acid aqueous solution, greater than 3 N approximately, preferably an aqueous solution of nitric acid in the case of cationic extraction agents.

The one or more extracted rare earths are recovered in the aqueous phase while the extracting solvent may be recycled to the extraction stage.

According to the invention, the neodymium or didymium can be separated in a number of ways. The order in which the separations take place are unimportant.

To separate the neodimium, this can be done according to sequence 1, separation of lanthanum-praseodymium from the mixture neodymium, yttric rare earths then separation of the neodymium from the yttric rare earths or according to sequence 2, separation of the ceric rare earths (La, Nd, Pr) from the yttric rare earths then separation of the lanthanum and the praseodymium from the neodymium.

More precisely, according to sequence 1, the aqueous solution of rare earth nitrates is placed in contact with the extraction solvent to extract in the organic phase the neodymium nitrates and the yttric rare earths and leave in the aqueous phase the lanthanum and praseodymium nitrates, counter-extracting the neodymium and yttric rare earth nitrates from the organic phase to recover them in the aqueous phase, placing this solution with an extracting agent to extract the yttric rare earth nitrates in the aqueous phase and leave the neodymium nitrate in the aqueous phase. With sequence 2 for the separation, the aqueous solution of rare earth nitrates is placed with the extracting solvent in order to extract in the organic phase, the yttric rare earth nitrates and leave in an aqueous phase the lanthanum, neodymium and praseodymium nitrates, placing this solution with an extracting solvent so as to extract the neodymium in an organic phase and leave the praseodymium and lanthanum nitrates in an aqueous phase, then counter-extracting the neodymium nitrate from the organic phase to recover it in an aqueous phase.

To obtain didymium, according to a first sequence a separation of the lanthanum from the mixture didymium-yttric
rare earths is carried out, then a separation of the didymium from the yttric rare earths, or according to a second sequence, separating the ceric rare earths (La, Nd, Pr) from the yttric rare earths, then separating the lanthanum from the didymium.

The neodymium and didymium solutions obtained in accordance with the method of the invention produce first class raw materials for the production of carbonates, chlorides, fluorides or oxides used as mediums, in particular in the manufacture of metals for magnets.

The examples which follow illustrate the invention without, however, placing any limits on it. In these examples the percentages given are expressed in weight.

**EXAMPLE 1:**

This example illustrates the selectivity of the solubilisation cerium/trivalent rare earths at the time of the careful lixiviation of a calcined bastnasite concentrate in accordance with the invention.

A concentrate of bastnasite ore [1] with the following ponderal composition is used:

- melting loss : 17.4 %
- CaO : 0.25 %
- P2O5 : 1.9 %
- BaO : 1.75 %
- F- : 5 %
- Fe2O3 : 0.3 %
- SiO2 : 0.1 %
- Al2O3 : 0.05 %
- total rare earth oxides : 74.5 %

distributed as follows:

CeO2 : 51.0 %
La2O3 : 32.0 %
Pr6O11 : 4.2 %
Nd2O3 : 11.8 %
Sm2O3 : 0.8 %
1 kg of basnasite is calcined in a muffle furnace for 3 hours at 700°C. 831 g of a calcined concentrate of bastnasite [2] is obtained having the following composition:

- melting loss : 0.6 %
- CaO : 0.3 %
- P2O5 : 2.3 %
- BaO : 2.1 %
- F- : 5.9 %
- total rare earth oxides : 89.6 %

100 g of this calcined bastnasite concentrated [2] is carefully lixiviated by treating it with 120 cm³ of 6.5 N nitric acid. This process takes place while being stirred at 60°C and the duration is 1 hour.

The solid residue is separated from the solution of rare earth nitrates by filtration through a Buchner. The solution which is recovered contains rare earths, the concentration of which in oxides is 370 g/l, 4.8 g/l of fluorine and 0.35 g/l of Fe2O3. The distribution of rare earths is the following:

CeO₂ : 6.0 %
La2O₃ : 60.3 %
Pr₆O₁₁ : 8.3 %
Nd2O₃ : 22.6 %
Sm₂O₃ : 1.6 %
other rare earths : 1.2 %

These results correspond to the rate of solubilisation of the rare earths contained in the bastnasite concentrate used in the first instance.

CeO₂ : 5.6 %
La₂O₃ : 90.6 %
Pr₆O₁₁ : 95.3 %
I should be noted that the solubilisation yield of the trivalent rare earths is 95.3% and that of cerium 5.6%.

It should also be noted that the soluble cerium is composed of 71.1% of cerium IV. The fluorine is only dissolved to 9.8%.

Example 2

A series of trials are done according to the method used in example 1 so as to show the effect of the quantity of nitric acid used on the selectivity cerium/rare earths.

To achieve this, 4 fractions of 100 g of calcined bastnasite concentrate from example 1 are used.

It is attacked in the same conditions as in example 1 by variable quantities of 6.5 N nitric acid, these are shown in table 1 which follows.

After separation of the residues and their analysis, the following rate of solubilisation is obtained:

<table>
<thead>
<tr>
<th>quantity of 6.5 N HNO₃</th>
<th>120 cm³</th>
<th>180 cm³</th>
<th>240 cm³</th>
<th>360 cm³</th>
</tr>
</thead>
<tbody>
<tr>
<td>concentration of the solution of rare earth nitrates given in total rare earth oxides (g/l)</td>
<td>370</td>
<td>310</td>
<td>340</td>
<td>240</td>
</tr>
<tr>
<td>solubilisation rate (%)</td>
<td>lanthanum</td>
<td>90.6</td>
<td>92.0</td>
<td>98.4</td>
</tr>
<tr>
<td>cerium</td>
<td>5.6</td>
<td>31.5</td>
<td>85.9</td>
<td>95.9</td>
</tr>
<tr>
<td>praseodymium</td>
<td>95.3</td>
<td>96.0</td>
<td>98.7</td>
<td>96.6</td>
</tr>
<tr>
<td>neodymium</td>
<td>92.1</td>
<td>90.7</td>
<td>90.9</td>
<td>96.7</td>
</tr>
<tr>
<td>trivalent rare earths</td>
<td>95.3</td>
<td>95</td>
<td>96.2</td>
<td>97</td>
</tr>
<tr>
<td>thorium</td>
<td>&lt;1</td>
<td>15</td>
<td>62.5</td>
<td>87.5</td>
</tr>
<tr>
<td>fluorine</td>
<td>9.8</td>
<td></td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>Ce IV/Ce total :</td>
<td>0.71</td>
<td>0.82</td>
<td>0.94</td>
<td>0.98</td>
</tr>
</tbody>
</table>
In view of the results obtained, the adequate quantity of acid corresponds to the stoichiometry of the trivalent rare earths.

EXAMPLE 3:

This example shows the influence of the concentration of nitric acid in relation to example 2.

The method is the same as for example 2 with the difference that the lixiviation of the calcined bastnasite concentrate is done with an aqueous solution of 3.5 N nitric acid.

The results obtained are shown in table II.

<table>
<thead>
<tr>
<th>quantity of 6.5 N HNO₃</th>
<th>220 cm³</th>
<th>340 cm³</th>
<th>450 cm³</th>
<th>670 cm³</th>
</tr>
</thead>
<tbody>
<tr>
<td>concentration of the solution of rare earth nitrates given in total rare earth oxides (g/l)</td>
<td>150</td>
<td>145</td>
<td>135</td>
<td>95</td>
</tr>
<tr>
<td>solubilisation rate (%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>lanthanum</td>
<td>75.8</td>
<td>94.9</td>
<td>95.1</td>
<td>96</td>
</tr>
<tr>
<td>cerium</td>
<td>0.1</td>
<td>16.7</td>
<td>41.1</td>
<td>45</td>
</tr>
<tr>
<td>praseodymium</td>
<td>83.9</td>
<td>95.3</td>
<td>95.3</td>
<td>95.5</td>
</tr>
<tr>
<td>neodymium</td>
<td>83.5</td>
<td>93</td>
<td>93.7</td>
<td>95.2</td>
</tr>
<tr>
<td>samarium</td>
<td>82.1</td>
<td>93.1</td>
<td>93.1</td>
<td>97</td>
</tr>
<tr>
<td>trivalent rare earths</td>
<td>75.5</td>
<td>93.3</td>
<td>95.4</td>
<td>96</td>
</tr>
<tr>
<td>thorium</td>
<td>&lt;1</td>
<td>12</td>
<td>50</td>
<td>63</td>
</tr>
</tbody>
</table>

A comparison between examples 1 and 2 shows that the concentration of the aqueous solution of nitric acid is not critical.

EXAMPLE 4:

This example illustrates the separation of the neodymium.

The bastnasite concentrated as defined in example 1 is calcined and carefully lixiviated as described in example 1.

When the process is finished, the solid residue
containing essentially the cerium of the aqueous solution of rare earth nitrates with a concentration in rare earth oxides of 370 g/l is separated by filtration.

The tetravalent cerium and the traces of thorium present are eliminated by adding an aqueous solution of ammonium hydroxide 10 N until a pH of 3.5 is obtained.

The remaining solid residue containing all the tetravalent cerium and thorium is separated by filtration. Analysis of this residue shows that it also contains 86 % fluorine and the almost complete totality of dissolved iron and 5 % of the trivalent rare earths.

The solution of rare earth nitrates recovered has a concentration of rare earth oxides of 337 g/l and contains 0.7 g/l of fluorine, less than 10 mg/l of Fe₂O₃ and less than 10 mg/l of ThO₂. The distribution of rare earths is the following:

- 63.0 % of La₂O₃
- 1.8 % of CeO₂
- 8.7 % of Pr₆O₁₁
- 23.6 % of Nd₂O₃
- 1.7 % of Sm₂O₃
- 1.3 % of the other rare earths.

This solution is concentrated by evaporation until a concentration in rare earth oxides of 490 g/l is obtained. This concentrated solution then undergoes liquid-liquid extraction using the method illustrated in figure 1.

The equipment used for separating the rare earths includes:

- a first liquid-liquid extraction battery with several stages of the mixing-decanting type operating at counter-flow and composed of an extraction section (a), a leaching section (a') with 40 theoretical stages and a counter-extraction section (b) of the rare earths extracted in the organic phase made up of 10 theoretical stages.

- a second liquid-liquid extraction battery composed of an extraction section (c) and a leaching section (c') composed of 40 theoretic stages and a counter-extraction section (d) of the rare earths extracted in the organic phase made up of
10 theoretical stages.

The extraction agent used is tributylphosphate. It is placed in solution in kerosene at 75% by volume and the mixture obtained will be referred to as the extraction solvent.

Before giving details of the various processes, it should be stated that for the entry and exit of the extraction-leaching and counter-extraction units, the direction of flow of the organic phase is used.

The aqueous solution of rare earth nitrates is introduced at 1 at the 20th stage of the extraction-leaching section at a rate of flow of 2.05 litres/hour.

At the entry of the extraction-leaching section, the organic phase composed of the extraction solvent is introduced at 2 at a rate of flow of 8.8 litres/hour.

At the outlet of the counter-extraction section and counter to the current of the organic phase, at 5, acidified water (HNO₃ - 0.1 N) is introduced at a rate of 4.4 litres/hour.

At the entry to counter-extraction section 6, an aqueous solution of rare earth nitrates is recovered, this contains the neodymium and the yttric rare earths which are concentrated by evaporation until a concentration expressed in rare earth oxides of 490 g/l is obtained. 0.54 litre/hour is taken off, this constitutes the production of neodyme concentrate and the rest 1.78 litres/hour supplies at 3 the extraction-leaching section to obtain a back-flow. The neodymium concentrate has a composition expressed in rare earth oxides as follows:

- 88.4% of Nd₂O₃
- 0.5% of Pr₆O₁₁
- 6.3% of Sm₂O₃
- 4.9% of other rare earths.

At the entry to the extraction-leaching section, at 4 an aqueous solution of rare earth nitrates is recovered, this is concentrated by evaporation until a concentration expressed in rare earth oxides of 490 g/l is obtained. 1.5 litres/hour is taken off, constituting the concentrated production of lanthanum the remainder is recycled at 2 at the first stage of the battery. This lanthenum concentrate has a composition expressed in rare
earth oxides made up as follows:
- 85.9% of La$_2$O$_3$
- 2.4% of CeO$_2$
- 11.7% of Pr$_6$O$_{11}$
- less than 0.01% of Nd$_2$O$_3$ and other rare earths.

At 7, the exit of the counter-extraction section, the regenerated extraction solvent is recovered, this can be recycled at 2 in the extraction-leaching section at the same flow rate.

The neodymium concentrate described above supplies the second liquid-liquid extraction battery. It is introduced at 8, at the 20th stage of the extraction-leaching section.

At the entry to the extraction-leaching section, at 9, the organic phase composed of the same extraction solvent is introduced at a flow rate of 3.15 litres/hour.

At 12, counter-current to the organic phase, acidified water is introduced at a flow rate of 1.6 litres/hour. At 13, a solution of rare earth nitrates is recovered, this is concentrated by evaporation until a concentration expressed in rare earth oxides of 490 g/l is obtained. 0.06 litre/hour is taken off which constitutes the production of an yttric rare earth concentrate and 0.78 litre/hour is recycled at 10 to create a back-flow. This yttric rare earth concentrate has a composition, expressed in rare earth oxides as follows:
- 56.2% of Sm$_2$O$_3$
- 43.7% of other rare earths
- 0.12% of Nd$_2$O$_3$

At the entry to the extraction-leaching section, at 11 an aqueous solution of neodymium nitrate is recovered and concentrated by evaporation until a concentration expressed in rare earth oxides of 490 g/l is obtained. 0.48 l/h of it is taken off, this constitutes the production of neodymium and the rest is recycled at 9 with the organic phase.

The purity of the neodymium produced is the following:
- 99.4% of Nd$_2$O$_3$
- 0.6% of Pr$_6$O$_{11}$
- less than 0.1% of the other rare earths.

At the exit to the counter-extraction section, at 14,
the regenerated extraction solvent is recovered, this may be recycled at 9 in the extraction-leaching section.

EXAMPLE 5:

This example illustrates the separation of the didymium.

In accordance with the methods of operation described in examples 1 and 4, the following procedure is carried out:
- calcination of the bastnasite concentrate described in example 1.
- careful lixiviation of the calcined bastnasite concentrate
- separation by filtration of the solid residue of the rare earth nitrate solution
- pre-neutralisation of this solution
- separation by filtration of the solid residue of the solution of rare earth nitrates
- concentration by evaporation of this solution until a concentration expressed in rare earth oxides of 490 g/l is obtained.

This concentrated solution then undergoes the successive processes of liquid-liquid extraction carried out in accordance with the method of application illustrated in figure 1.

The equipment used for the separation of the rare earths includes:
- a first liquid-liquid extraction battery composed of an extraction section (a) a leaching section (a') which includes 48 theoretical stages and a counter extraction section (b) of the rare earths extracted in the organic phase having 10 theoretical stages.
- a second liquid-liquid extraction battery made up of an extraction section (c) and a leaching section (c') having 48 theoretical stages and a counter-extraction section (d) for the rare earths extracted in the organic phase and having 10 theoretical stages.

The extraction agent used is tributylphosphate placed in solution in kerosene at 75 % by volume.

The following describes the sequence of the various stages:

The aqueous solution of rare earth nitrates is introduced at 1 at the 20th stage of the extraction-leaching section at a rate of flow of 2.05 litres/hour.

At the entry to the extraction-leaching section, at 2,
the organic phase composed of the extraction solvent is introduced at a rate of flow of 11.1 litres/hour.

At 5, at the outlet of the counter-extraction section, at counter flow to the organic phase, acidified water (HNO₃ - 0.1 N) is introduced at a rate of 5.6. litres/hour.

At the entry to counter-extraction section 6, an aqueous solution of rare earth nitrates is recovered, it contains didymium and yttric rare earths which are concentrated by evaporation until a concentration expressed in rare earth oxides of 490 g/l is obtained. 0.72 litre/hour is taken off, this constitutes the production of the didymium concentrate and the rest, 0.89 litre/hour supplies the extraction/leaching section at 3 to create a back flow. The deodymium concentrate has a composition expressed in rare earth oxides of:

- 24.6 % of praseodymium
- 66.8 % of neodymium
- at least 0.01 % of cerium
- 8.5 % of other rare earths.

At the entry to the extraction-leaching section at 4, an aqueous solution of rare earth nitrates is recovered, this is concentrated by evaporation until a concentration expressed in rare earth oxides of 490 g/l is obtained. 1.32 litres/hour which constitutes the production of a lanthanum concentrate is taken off and the rest is recycled at 2 at the first stage of the battery. This lanthanum concentrate has a composition, expressed in rare earth oxides as follows:

- 97.2 % La₂O₃
- 2.7 % CeO₂
- less than 0.1 % of Pr₆O₁₁ and other rare earths.

The regenerated extraction solvent is recovered at 7, at the outlet of the counter-extraction section and may be recycled at 2 in the extraction-leaching section at the same rate of flow.

The deodymium concentrate defined above, constitutes the feed for the second liquid-liquid extraction battery. It is introduced at 8, at the 22nd stage of the extraction-leaching section.

At the entry to the extraction-leaching section, at 9, the organic phase composed of the same extraction solvent is introduced at a flow rate of 3.1 litres/hour.
At 12, counter flow to the organic phase, acidified water is introduced at a rate of 1.55 litres/hour.

At 13, a solution of rare earth nitrates is recovered and it is concentrated by evaporation until a concentration expressed in rare earth oxides of 490 g/l. is obtained. 0.60 litre/hour is taken off, this represents the production of a concentrate of yttric rare earths and 0.78 litre/hour is recycled at 10 to form the back flow. This yttric rare earth concentrate has a composition, expressed in rare earth oxides of:

- 56.2 % Sm\textsubscript{2}O\textsubscript{3}
- 43.6 % of other rare earths
- 0.19 % Nd\textsubscript{2}O\textsubscript{3}

At the entry to the extraction-leaching section, at 11 an aqueous solution of neodymium and praseodymium nitrate is recovered, this is concentrated by evaporation until a concentration in oxides of rare earths of 490 g/l is obtained. 0.66 l/h are taken off, this constituting the production of didymium and the rest is recycled at 9 with the organic phase.

The quality of the didymium produced is the following:

- 26.9 % Pr\textsubscript{6}O\textsubscript{11}
- 73.1 % Nd\textsubscript{2}O\textsubscript{3}
- less than 0.01 % of other rare earths.

At 14, the outlet of the counter-extraction section, the regenerated extraction agent is recovered and can be recycled at 9 in the extraction-leaching section.
THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:-

1. A method for the separation of neodymium or didymium from rare earths contained in bastnasite, characterised by the steps of:
   - calcination of the bastnasite,
   - lixiviation of the calcined bastnasite with a nitric acid solution so as to dissolve the neodymium and the trivalent rare earths but not any cerium and traces of thorium which are present in the form of an insoluble residue,
   - separation and purification of the neodymium or didymium by liquid-liquid extraction between the aqueous phase composed of the aqueous solution of rare earth nitrates recovered at the previous stage and an organic phase containing an extraction agent, insoluble in water, then recovering the neodymium or didymium from the organic phase.

2. A method according to claim 1, characterised by the fact that the bastnasite contains more that 10 % by weight of rare earth expressed as rare earth oxides.

3. Method according to claim 1, characterised by the bastnasite being concentrated and containing from 40 to 75 % by weight of rare earth expressed as rare earth oxides.

4. A method according to one of the claims 1 to 3, characterised by the calcination temperature being higher than 400°C.

5. A Method according to claim 4, characterised by the calcination temperature being included between 600 and 800°C.
6. A method according to one of the claims 4 and 5 characterised by the duration of the calcination varying between 30 minutes and 3 hours.

7. A method according to one of the claims 1 to 6 characterised by the careful lixiviation being done with a nitric acid solution with a concentration of 1 to 14 N.

8. A method according to claim 7 characterised by the careful lixiviation being carried out with a nitric acid solution with a concentration of 3 to 9 N.

9. A method according to one of claims 1 to 8 characterised by the quantity of nitric acid used being equal to a quantity from the stoechiometric quantity of the trivalent rare earths to an excess which may reach 50 % of the stoechiometric quantity.

10. A method according to one of the claims 7 to 9 characterised by the lixiviation being carried out at between 20 and 90°C.

11. A method according to claim 10, characterised by the time spent in the lixiviation solution being between 30 minutes and 2 hours.

12. A method according to one of the claims 1 to 11 characterised by the lixiviation being carried out at 60°C for a duration of one hour.

13. A method according to one of the claims 1 to 12 characterised by the insoluble residue being separated from the lixiviation solution.

14. A method according to one of the claims 1 to 13 characterised by the lixiviation solution containing more than 90 % of trivalent rare earths including neodymium and
less than 10 % of the cerium initially present in the bastnasite.

15. A method according to claim 14 characterised by the concentration of rare earths expressed in oxides of rare earths being between 150 and 500 g/l.

16. A method according to one of the claims 1 to 15 characterised by carrying out a pre-neutralisation by the addition of a base to the solution of rare earth nitrates until pH between 2 and 4 is obtained, this allowing for the elimination of the fluorine, the cerium and traces of thorium in a solid residue which is then separated.

17. A method according to claim 1 characterised by the extraction agent used being a solvating extraction agent.

18. A method according to claim 17 characterised by the extraction agent being tributylphosphate.

19. A method according to any one of the preceding claims further including the step of separating cerium from said insoluble residue.

20. A method substantially as herein described with reference to the examples.

DATED this 17th day of March, 1987

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