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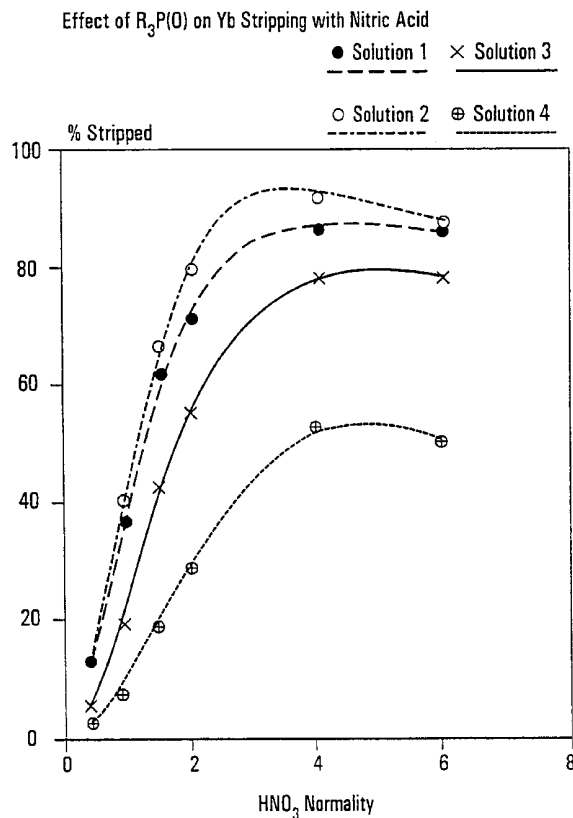
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(54) Title: STRIPPING LANTHANIDE-LOADED PHOSPHONIC/PHOSPHINIC EXTRACTANT SOLUTIONS IN THE PRESENCE OF PHOSPHINE OXIDE



(57) Abstract: Using an organophosphonic/organothiophosphonic acid, and optionally, an organophosphinic/organothiophosphinic acid as extractant, efficiency of stripping of lanthanide is improved by varying the concentration of phosphine oxides or esters of phosphorus in the extraction solution. Namely, the stripping efficiency of hydrochloric acid is increased by adding or increasing the concentration of phosphine oxide or ester of phosphorus in the extractant solution; and the stripping efficiency of nitric acid is increased by removing or decreasing the concentration of phosphine oxide or ester of phosphorus in the extractant solution.

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STRIPPING LANTHANIDE-LOADED PHOSPHONIC/PHOSPHINIC EXTRACTANT SOLUTIONS IN THE PRESENCE OF PHOSPHINE OXIDE

FIELD OF THE INVENTION

This invention relates to a method for stripping lanthanide-loaded solvent.

BACKGROUND OF THE INVENTION

The lanthanides, also known as the rare earths, comprise elements 57 to 71 of the Periodic Table. Depending upon the atomic number of the element, this series is often divided into three sub-groups i.e. the light, medium and heavy rare earths. The lightest is lanthanum with atomic number 57. In contrast, the four heavy rare earths are erbium, thulium, ytterbium, and lutetium with atomic numbers of 68, 69, 70, and 71, respectively. Scandium, atomic number 21, and yttrium, atomic number 39, are often found with, and discussed with, the lanthanides. In nature, they are generally found in their oxide form, and are commercially isolated from *monazite*, *xenotime*, *bauxite*, and *bastnasite*, or similar ores. Their isolation, wherein the elements are recovered together or separated from one another, has become of importance in recent years.

One source of lanthanides is red mud that is produced as a by-product of the Bayer process for producing alumina. The Bayer process for producing alumina comprises, as its first step, leaching or digesting bauxite or similar crude ores with a solution of sodium hydroxide to extract alumina minerals contained therein as a solution of sodium

aluminate. At the same time, as much as one third to one half of the total weight of the crude ore used is discharged as a residual red mud. This red mud typically contains substantial amounts of silica, alumina, iron oxide, titania and sodium compounds. Many red muds also contain small but valuable quantities of lanthanide elements, and in some cases include significant quantities of scandium and yttrium. If the red mud is digested with dilute mineral acid, the lanthanide elements, and scandium and yttrium, selectively dissolve in the acid, together with sodalite and calcium compounds, leaving iron and titanium in the red mud substantially undissolved. Examples of suitable acids include hydrochloric, nitric, sulphuric, and sulphurous acids.

The first general separation procedures, introduced in the 1950s, were based on complexation-enhanced ion exchange processes. However, in the 1960s liquid-liquid extraction processes were introduced and these types of processes are generally used in large-scale commercial production today.

One procedure employed, especially for the separation of lanthanides from aqueous hydrochloric and nitric acid solutions, is as follows. The aqueous acidic lanthanide solution is contacted counter-currently or co-currently with an extractant solution comprising a water-immiscible organic solvent containing the mono-2-ethylhexyl ester of mono-2-ethylhexylphosphonic acid, known as MEPA, or di(2-ethylhexyl) phosphoric acid, known as DEPA. The lanthanide is extracted from the aqueous acidic solution into the water-immiscible

organic solvent. The organic solution containing the extracted lanthanide(s) is then stripped with an acid such as hydrochloric, nitric, or sulphuric acid to remove the lanthanide(s) from the organic solution. The lanthanide passes into the acidic aqueous solution and is then precipitated from the acidic solution, for example as a hydroxide, oxalate or carbonate, by the addition of a neutralizing or precipitating agent.

One problem, particularly in regard to the heavy
10 lanthanides, namely erbium, thulium, ytterbium, and lutetium, is that they are very strongly complexed by the organophosphorus extractant during the extraction process, and as a result require a greater concentration of acid in the stripping process. This is also true of scandium and yttrium. The need for a greater concentration of acid results in increased processing costs because large quantities of acid have to be neutralized. In the case of stripping with hydrochloric acid, it can also result in contamination of the final product by chloride ions. In addition, use of highly
20 concentrated acid is undesirable for safety reasons.

There have been some attempts to improve the stripping efficiency. U.S. Patent 5,639,433 teaches the use of an extractant solution containing an organophosphonic acid, such as MEPA, in combination with an organophosphinic acid, such as bis(2,4,4-trimethylpentyl)phosphinic acid (BTPP) for the extraction of rare earths. An advantage obtained is that the lanthanide(s) are then more readily stripped from the

solution.

BTPP is commercially available from Cytec as CYANEX™ 272, but this product also contains tris(2,4,4-trimethylpentyl)phosphine oxide, in an amount of approximately 12-14%, and mono-2,4,4-trimethyl-pentylphosphonic acid, in an amount of approximately 1%. Thus, there is present about 13.8% to about 16.5% of tris-(2,4,4-trimethylpentyl)phosphine oxide, based on the amount of BTPP.

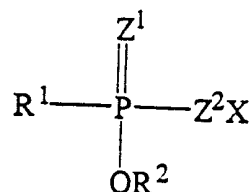
SUMMARY OF THE INVENTION

10 It has now surprisingly been found that the presence of a phosphine oxide or an ester of phosphorus in the extractant solution affects the efficiency of stripping by hydrochloric and nitric acid.

In one aspect this invention provides a process for stripping a lanthanide from a lanthanide-containing extractant solution which process comprises:

(a) contacting the lanthanide-containing extractant solution with aqueous hydrochloric acid to strip the lanthanide into the aqueous hydrochloric acid, wherein the
20 extractant solution contains the lanthanide and further comprises:

- (i) a water-immiscible diluent,
- (ii) an organophosphonic acid or an organo-thiophosphonic acid of formula



wherein

10 R^1 and R^2 may be the same or different and each represents a C_4 -12 substituted or unsubstituted alkyl group or a C_4 -8 substituted or unsubstituted cycloalkyl group, or a substituted or unsubstituted phenyl group,

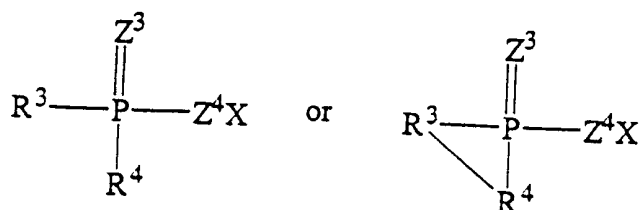
Z^1 and Z^2 may be the same or different and each represents oxygen or sulphur, and

X represents hydrogen or a salt-forming radical,

that is soluble in the water-immiscible diluent, optionally

(iii) an organophosphinic acid or an organothiophosphinic acid of formula

20



wherein

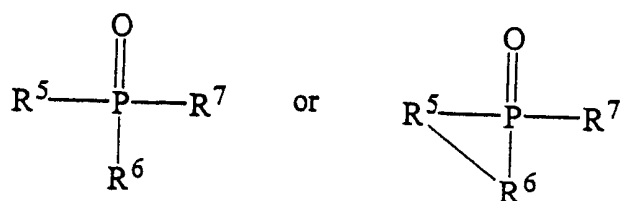
R^3 and R^4 may be the same or different and each represents a C_{4-12} substituted or unsubstituted alkyl group or C_{4-8} substituted or unsubstituted cycloalkyl group, or a substituted or unsubstituted phenyl group,

Z^3 and Z^4 may be the same or different and each represents oxygen or sulphur, and

10 X represents hydrogen or a salt-forming radical,

that is soluble in the water-immiscible diluent,

(iv) a phosphine oxide or an ester of phosphorus of formula



20 wherein R^5 , R^6 , and R^7 may be the same or different and each represents a C_{4-12} substituted or unsubstituted alkyl, alkoxy, cycloalkyl, cycloalkoxy group, or a substituted or unsubstituted phenyl group, provided that the number of carbons in R^5 ,

R^6 , and R^7 together total at least 18, and that is soluble in the water-immiscible diluent, and with the proviso that if component (ii) is the mono-2-ethylhexyl ester of mono-2-ethylhexylphosphonic acid,

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component (iii) is bis(2,4,4-trimethylpentyl)phosphinic acid, and the sole component (iv) is tris(2,4,4-trimethylpentyl)phosphine oxide, then the amount of tris(2,4,4-trimethylpentyl)phosphine oxide is greater than 16.5%, based on the amount of bis(2,4,4-trimethylpentyl)phosphinic acid; or

(b) contacting the lanthanide-containing extractant solution with aqueous nitric acid to strip the lanthanide into the aqueous nitric acid, wherein the extractant solution contains the lanthanide and further comprises components (i),
10 (ii), and (iii) and optionally component (iv), with the proviso that if component (ii) is the mono-2-ethylhexyl ester of mono-2-ethylhexylphosphonic acid, and component (iii) is bis(2,4,4-trimethylpentyl)phosphinic acid, then tris(2,4,4-trimethylpentyl)phosphine oxide is present in an amount not greater than 13.8%, based on the amount of bis(2,4,4-trimethylpentyl)phosphinic acid, preferably not greater than about 10% and, most preferably, is absent.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a graph showing the effect of phosphine
20 oxide concentration on the stripping of Yb with hydrochloric acid using 0.5 M of organophosphonic acid and 0.5 M of organophosphinic acid.

Figure 2 is a graph showing the effect of phosphine oxide concentration on the stripping of Yb with nitric acid using 0.5 M of organophosphonic acid and 0.5 M of organophosphinic acid.

Figure 3 is a graph showing the effect of phosphine

oxide concentration on the stripping of Yb with hydrochloric acid using 0.75 M of organophosphonic acid and 0.75 M of organophosphinic acid.

Figure 4 is a graph showing the effect of phosphine oxide concentration on the stripping of Yb with nitric acid using 0.75 M of organophosphonic acid and 0.75 M of organophosphinic acid.

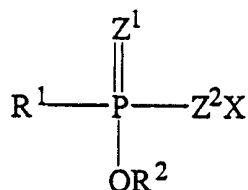
DESCRIPTION OF PREFERRED EMBODIMENTS OF THE INVENTION

Using an organophosphonic/organothiophosphonic acid,
10 and, optionally, an organophosphinic/organothio-phosphinic acid as the extractant, the Applicant has now demonstrated that the efficiency of stripping can be improved by varying the concentration of phosphine oxide or ester of phosphorus in the extractant solution. Namely, the stripping efficiency of hydrochloric acid is increased by adding or increasing the concentration of phosphine oxide or ester of phosphorus in the extractant solution; and the stripping efficiency of nitric
20 acid is increased by removing or decreasing the concentration of phosphine oxide or ester of phosphorus in the extractant solution.

The extractant solution from which the lanthanide is to be stripped is usually a solution that has been obtained by subjecting an aqueous acid leachate of a lanthanide-containing ore to extraction with an organophosphorus-containing organic extractant. The leachate is usually a very weakly acidic solution, say about pH 2 to about 5, that is contacted, co-currently or countercurrently, with the extractant, causing

lanthanides to be extracted from the weakly acidic aqueous solution into the organophosphorus-containing organic extractant. The relative volume of the aqueous acidic leachate containing the lanthanide to the organic extractant can vary between wide limits; it may depend, for instance, upon the particular arrangements at an extraction plant or mine. Ratios from about 20:1 to about 1:20, particularly from about 10:1 to about 1:10 are mentioned.

The extractant solution includes an organo-
10 phosphonic or organothiophosphonic acid of formula:



wherein R^1 and R^2 may be the same or different and each represents C_4 - 12 , preferably C_6 - 10 , substituted or unsubstituted alkyl group or a C_4 - 8 , preferably C_5 or C_6 ,
20 substituted or unsubstituted alkyl group, cycloalkyl group, or a substituted or unsubstituted phenyl group, and Z^1 and Z^2 may be the same or different and each represents oxygen or sulphur. Preferably Z^1 is oxygen; more preferably both Z^1 and Z^2 are oxygen. X is hydrogen or a salt-forming radical; preferably, X is hydrogen, an alkali metal, or ammonium ion. Mixtures of such compounds can be used.

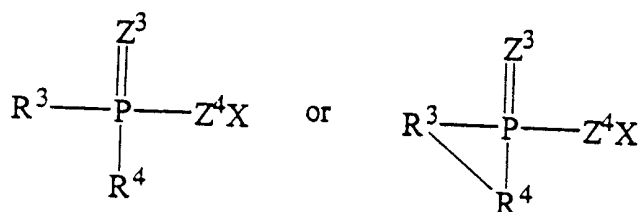
Examples of suitable organophosphonic and

organothiophosphonic acids include the mono-2-ethylhexyl ester of mono-2-ethylhexyl phosphonic acid; the cyclohexyl ester of 3,3,5-trimethylhexylphosphonic acid; the cyclopentyl ester of 2-ethylhexylphosphonic acid; the mono-2-ethylhexyl ester of phenylphosphonic acid; the mono-3-methyloctyl ester of n-amylphosphonic acid; the 3,5,5-trimethylhexyl ester of 3,3,5-trimethylhexylphosphonic acid; the monoisodecyl ester of 2-ethylhexylphosphonic acid; the monoisodecyl ester of isodecylphosphonic acid; the monoisodecyl ester of isodecylphosphonic acid and the like, and also the corresponding thio compounds. Especially preferred is the mono-2-ethylhexyl ester of mono-2-ethylhexylphosphonic acid.

The organophosphonic or organothiophosphonic acid component is suitably present in an amount of 0.1 - 1M, preferably 0.25 - 0.75M, more preferably about 0.4 - 0.6M in the solution to be stripped.

The extractant solvent further, optionally, includes an organophosphinic or organothiophosphinic acid of formula:

20



wherein R^3 and R^4 may be the same or different and each represents a C_4 -12, preferably C_6 -10, substituted or unsubstituted alkyl group or a C_4 -8, preferably C_5 or C_6 , substituted or unsubstituted cycloalkyl group, or a

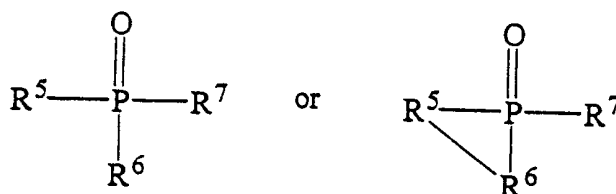
substituted or unsubstituted phenyl group, and Z^3 and Z^4 may be the same or different and each represents oxygen or sulphur, X represents hydrogen or a salt-forming radical, preferably hydrogen alkali metal, or ammonium ion. Mixtures of such compounds can be used.

U.S. Pat. Nos. 4,348,367 and 4,353,883 disclose suitable phosphinic acids and salts and are incorporated herein by reference. Examples of suitable organophosphinic acids include the following: di-n-butylphosphinic acid; di-
10 isobutylphosphinic acid; di-n-pentylphosphinic acid; di-n-hexylphosphinic acid; di-heptylphosphinic acid; di-n-octylphosphinic acid; bis(2-ethylhexyl)phosphinic acid; di-n-nonylphosphinic acid; di-n-decylphosphinic acid; di-n-dodecylphosphinic acid; bis(2,4,4-trimethylpentyl)phosphinic acid; (2,4,4-trimethylpentyl)cyclohexylphosphinic acid; (2,4,4-trimethylpentyl)octylphosphinic acid; dicyclo-
pentylphosphinic acid; dicyclohexylphosphinic acid; dicyclooctylphosphinic acid; cyclohexyl-n-butylphosphinic acid; cyclopentyl-n-dodecylphosphinic acid; cyclooctyl-
20 ethylphosphinic acid; 2,4,6-triisopropyl-1,3,5,-dioxaphosphodane-5-hydroxy-5-oxide phosphinic acid; cyclohexyl-1-hydroxycyclohexylphosphinic acid; bis(2-methyl-1-hydroxypentyl)phosphinic acid; cyclohexyl-1-hydroxycyclopentylphosphinic acid; (1-methylpentyl)-(1-hydroxy-1-methylpentyl)phosphinic acid; (1-hydroxy-1-methyl-ethyl)isopropylphosphinic acid, and the like, and the corresponding thio compounds.

Especially preferred is bis(2,4,4-trimethylpentyl)-phosphinic acid.

When using hydrochloric acid to strip, the extractant solution may contain no phosphinic acid derivative, i.e., no component (iii). It is preferred, however, that a phosphinic acid derivative shall be present. A suitable amount is from about 0.1 to about 1M, preferably 0.25 - 0.75M, more preferably about 0.4 - 0.6M in the extractant solution.

The extractant solution may optionally contain a
 10 component (iv), a phosphine oxide or ester of phosphorus of formula:



wherein R⁵, R⁶, and R⁷ may be the same or different and each represents C₄₋₁₂, preferably C₆₋₁₂, substituted or unsubstituted alkyl, alkoxy, C₄₋₈, preferably C₅₋₆,
 20 cycloalkyl, cycloalkoxy group, or a substituted or unsubstituted phenyl or phenoxy group provided that the number of carbon atoms present in R⁵, R⁶, and R⁷ together total at least 18. Mixtures of phosphine oxides or phosphorus esters can be used.

When none of R⁵, R⁶, and R⁷ is alkoxy, cycloalkoxy or phenoxy, then the component (iv) is a phosphine oxide. When one of R⁵, R⁶ and R⁷ is alkoxy, cycloalkoxy or phenoxy

then the component (iv) is a phosphinate ester. When two of R⁵, R⁶ and R⁷ are alkoxy, cycloalkoxy or phenoxy then the component (iv) is a phosphonate ester. When three of R⁵, R⁶ and R⁷ are alkoxy, cycloalkoxy or phenoxy then the component (iv) is a phosphate ester. Any of these, or mixtures of these, can be used as component (iv), but it is preferred that component (iv) is a phosphine oxide. Particularly preferred as component (iv) are tri-n-octylphosphine oxide (TOPO), tris(2,4,4-trimethylpentyl)phosphine oxide (TTMPP) and
10 trihexylphosphine oxide.

Strictly, the term lanthanide includes elements 57 to 71 of the Periodic Table. The process of the invention is more effective with lanthanides of atomic numbers 65 to 71 inclusive, and especially with those of atomic numbers 69 to 71. These are the lanthanides that complex most strongly with the organophosphorus extractant, as stated above. As also stated above, scandium and yttrium are often found with lanthanides and the process of the invention is effective with scandium and yttrium; in their stripping properties, these two
20 elements are similar to the heavy lanthanides. In the description of the invention the term "lanthanide" should be understood to include scandium and yttrium unless the context requires otherwise. The concentration of the lanthanide in the extractant solution may vary between wide limits, but is suitably about 0.005M to about 0.2M, preferably about 0.05M to about 0.15M.

When the extractant solution is to be stripped with

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hydrochloric acid, the concentration of component (iv) is preferably about 0.05M to about 0.6M, more preferably about 0.1M to about 0.4M, most preferably about 0.15M to about 0.25M, and especially 0.2M. Component (iv) is preferably a phosphine oxide, but it is in accordance with the invention that some or all of component (iv) is an ester of phosphorus. It has been found that the use of phosphine oxide or ester of phosphorus at these concentrations permits use of lower concentrations of hydrochloric acid for the stripping than typically used in the prior art. Consequently, the concentration of hydrochloric acid used for the stripping is preferably about 0.5 N to about 4 N, more preferably about 1 N to about 3 N, most preferably about 1.2 N to about 1.8 N.

When using hydrochloric acid for stripping, good results can be obtained from an extractant solution that does not contain a phosphinic acid derivative, i.e., does not contain a component (iii). It is preferred that the phosphinic acid derivative is present, however.

When the extractant solution is to be stripped with nitric acid, component (iv) is preferably absent, or is present in an amount not exceeding about 0.1 M. This permits use of lower concentrations of nitric acid for the stripping than typically used in the prior art. Consequently, the concentration of nitric acid used for the stripping is preferably about 0.5 N to about 4 N, more preferably about 1 N to about 3 N, most preferably about 1.7 N to about 2.3 N.

The extractant solution contains a water-immiscible

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diluent, as component (i). Examples of useful diluents include halogenated and non-halogenated aliphatic and aromatic hydrocarbons such as, for example, hexane, heptane, octane, dodecane, benzene, toluene, xylenes, ethylbenzene, and the corresponding chlorinated compounds and petroleum cuts such as kerosene, fuel oil, JP-1, aliphatic hydrocarbons available under the trade-mark EXXSOL D-80, and the like. Components (ii), (iii) and (iv) are soluble in the diluent.

The temperature at which the lanthanide is stripped
10 by the acid is not critical. It may range from about 10°C to about 80°C, preferably from about 15°C to about 70°C, most preferably from about 20°C to about 60°C.

The ratio of acid to extractant solution can vary between wide limits and, for example, may range from 20:1 to 1:20, particularly 10:1 to 1:10.

The aqueous leachate from which the lanthanide is extracted into the extractant solution should be acidic, i.e. the pH should be under about 6.5, preferably from about 1 to 4. If necessary or desirable the pH can be adjusted by
20 addition of a suitable reagent, for example aqueous sodium hydroxide or ammonia.

After stripping, the lanthanide may be isolated by precipitation, for example, using a base to precipitate a hydroxide or carbonate, from the aqueous hydrochloric or nitric acid used to strip. Alternatively, the lanthanide can be precipitated by addition of oxalic acid or an oxalate salt.

In the case where the lanthanide-containing

extractant solution is obtained by extracting the lanthanide from an aqueous acidic leachate, it is possible to include in the process a scrubbing step before the extractant solution is stripped by treatment with hydrochloric or nitric acid. The scrubbing can be carried out by washing with a dilute aqueous solution of a mineral acid, for example hydrochloric, nitric, phosphoric or sulphuric acid. The solution is only weakly acidic, so the lanthanide is not stripped from the organic phase into the aqueous phase during this scrubbing step. As a
10 further aid to preventing loss of lanthanide into the scrubbing solution, the scrubbing solution may contain a lanthanide so that partition between the organic and aqueous solutions does not cause lanthanide from the organic solution to enter the aqueous scrubbing solution.

After the extractant solution has been stripped of lanthanide, it can be recycled for re-use to extract more lanthanide from an aqueous acidic leachate from a lanthanide-containing ore. Before recycling the stripped solution, it may be desirable to wash the solution. For this purpose
20 strong aqueous mineral acid, for instance hydrochloric, nitric, or sulphuric acid of pH less than about 1, preferably less than about 0.5 is suitable. The acid used for this washing should be stronger than the acid used for stripping.

The invention is further illustrated in the following non-limiting examples.

Example 1

Solutions from which a lanthanide was stripped were

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prepared using commercial grade CYANEX™ 272, purified CYANEX 272, IONQUEST™ 801, and tri-n-octylphosphine oxide (TOPO). EXXSOL™ D-80 was used as diluent.

Commercial grade CYANEX 272 contains 85-87% bis(2,4,4-trimethylpentyl)phosphinic acid (BTPP): and 12-14% tris(2,4,4-trimethylpentyl)phosphine oxide (TTMPP), i.e. the amount of tris(2,4,4-trimethyl-pentyl)phosphine oxide is about 13.8 to 16.5%, based on the amount of BTPP.

Purified CYANEX 272 contains greater than 99%
10 bis(2,4,4-trimethylpentyl)phosphinic acid (BTPP).

IONQUEST 801 contains 97% mono-2-ethylhexyl ester of mono-2-ethylhexylphosphonic acid (MEPA).

EXXSOL D-80 is composed of a mixture of C₁₀-C₁₂ hydrocarbons.

Nine different extractant solutions were prepared, the compositions of which are shown in Table 1. The solutions were washed with hydrochloric acid (100 g/L HCl) (ratio of aqueous to organic phase (A/O) is 1, at 24°C) and then with deionised water (A/O=1, at 24°C) and then centrifuged to remove
20 entrained water before use.

A lanthanide-loaded solution was prepared by contacting the washed extractant solution with an aqueous solution of 0.1M Yb(3+) chloride at pH = 3 and 24°C for 10 minutes. Sodium hydroxide (100 g/L NaOH) was used for pH control. The loaded extractant solution was centrifuged and the concentration of Yb loaded was determined, by Inductively

Coupled Plasma (ICP) analysis, to be 0.09 to 0.1M.

Aliquots of the loaded solution were contacted with aliquots of HCl (0.5 to 6N) for 25 minutes at room temperature and A/O=1, to investigate strippability. After phase separation, the aqueous solutions (strip liquors) were centrifuged to remove entrained organic material and were analysed for Yb by ICP. The percentage of Yb stripped was calculated by mass balance, using the known concentration of Yb in the loaded solution.

10 **Example 1(a):** Solutions 1 to 4 contained 0.5M of BTTP (an organophosphinic acid), 0.5M MEPA (an organophosphonic acid) and phosphine oxide in concentrations of 0.08M, 0M, 0.2M and 0.4M, respectively. Using hydrochloric acid to strip Yb from the loaded solution 3 or 4 is in accordance with the invention. Using hydrochloric acid to strip solution 1 or 2 is not in accordance with the invention; these are comparative examples.

For solutions 1 to 4, the effect of HCl concentration on Yb stripping is shown in Table 2 and plotted
20 in Figure 1. As is shown clearly in Figure 1, when using hydrochloric acid at lower concentration up to about 2N, Yb is more readily stripped from solutions 3 and 4 than from solutions 1 and 2.

Example 1(b): Solutions 5 to 7 contained 0.75M of BTTP, 0.75M of MEPA and concentrations of phosphine oxide of 0M, 0.11M and 0.2M, respectively. Use of solutions 5 and 6 is not in accordance with the invention when stripped with HCl.

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Use of solution 7 is in accordance with the invention when stripped with HCl.

For solutions 5 to 7, the effect of HCl concentration on Yb stripping is shown in Table 2 and plotted in Figure 3. These results show, for stripping with HCl, an increase in stripping efficiency for concentrations up to 2N HCl as the amount of phosphine oxide in the solution increases.

Example 1(c): Solutions 8 and 9 contain 0.75M of
10 MEPA, no phosphinic acid, and concentrations of phosphine oxide of 0M and 0.2M, respectively. As seen from Table 2, stripping efficiency improves at low concentrations of HCl, even in the absence of phosphinic acid. However, the stripping of Yb from solutions 8 and 9 with HCl is more difficult in the absence of phosphinic acid. Use of solution 9 is in accordance with the invention when stripped with HCl.

Thus, the invention permits use of hydrochloric acid of lower concentration, realizing the advantages and avoiding the disadvantages discussed above.

20 **Example 2**

Similar experiments were carried out using solvents 1 to 7 described in Example 1 and nitric acid to strip Yb from the loaded solution. The results are given in Table 3.

Example 2(a) For solutions 1 to 4, the effect of HNO
3 concentration on Yb stripping is plotted in Figure 2. Using nitric acid to strip Yb from the loaded solution 2 is in accordance with the invention. Using nitric acid to strip

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solutions 1, 3 and 4 is not in accordance with the invention; these solutions are comparative examples. As is shown clearly in Figure 2, with nitric acid Yb is more readily stripped from solution 2, especially at lower concentrations of nitric acid, up to about 2N.

Example 2(b) For solutions 5 to 7, the effect of HNO_3 concentration on Yb stripping is plotted in Figure 4. Use of solutions 6 and 7 with HNO_3 is not in accordance with the invention. Use of solution 5 with HNO_3 is in accordance
10 with the invention.

Example 3

Stripping experiments similar to those reported in Examples 1(a) and 2(a) were performed with another lanthanide element, lutetium, with essentially equivalent results.

Table 1: Comparison of various solutions prepared.

Solution #	Purified Cyanex 272 <u>BTTP</u>	Commercial Cyanex 272 <u>BTTP</u>	<u>TTMPP</u>	Ionquest 801 <u>MEPA</u>	<u>TOPO</u>
1	0	0.5M	0.08M	0.5M	0
2	0.5M	0	0	0.5M	0
3	0.5M	0	0	0.5M	0.2M
4	0.5M	0	0	0.5M	0.4M
5	0.75M	0	0	0.75M	0
6	0	0.75M	0.11M	0.75M	0
7	0.75M	0	0	0.75M	0.2M
8	0	0	0	0.75M	0
9	0	0	0	0.75M	0.2M

Table 2: Ytterbium Stripping with Hydrochloric Acid

	% Stripped from Solution #								
<u>HCl</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>	<u>9</u>
0.5 N	19.4	16.8	29.8	37.6	5.2	7.9	10.3		
1.0 N	48.7	42.2	57.2	70.6	29.0	34.3	40.4	8.0	15.1
1.5 N	81.2	66.8	86.2	89.6	57.0	58.4	65.8		
2.0 N	89.4	82.6	94.8	93.9	77.5	75.7	78.5	21.5	27.1
4.0 N	106.9	98.7	102.1	95.0	100	95.7	94.2		
6.0 N	98.0	100.8	98.2	96.4	100	96.4	92.7		

Table 3: Ytterbium Stripping with Nitric Acid

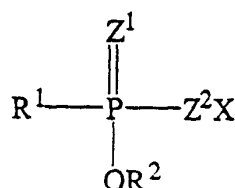
<u>HNO₃</u>	% Stripped from Solution #						
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>
0.5 N	13.1	13.0	4.8	1.9	4.3	5.4	2.4
1.0 N	36.6	39.6	19.4	6.9	22.3	23.4	11.9
1.5 N	61.7	66.7	42.3	19.0	44.8	41.8	25.3
2.0 N	71.6	80.1	55.1	29.2	59.7	54.8	36.2
4.0 N	87.0	92.3	78.4	53.1	78.1	74.6	57.9
6.0 N	86.7	88.4	78.8	50.7	75.8	72.4	

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A process for stripping a lanthanide from a lanthanide-containing extractant solution which process comprises:

(a) contacting the lanthanide-containing extractant solution with aqueous hydrochloric acid to strip the lanthanide into the aqueous hydrochloric acid, wherein the extractant solution containing the lanthanide also comprises:

- (i) a water-immiscible diluent,
- (ii) an organophosphonic acid or an organothiophosphonic acid of formula



wherein

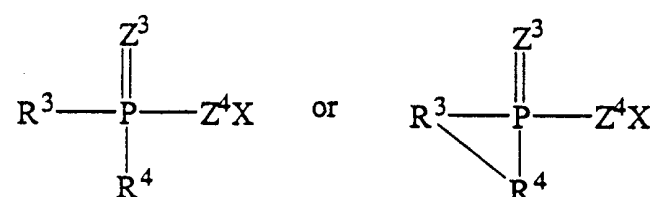
R^1 and R^2 may be the same or different and each represents a C_{4-12} substituted or unsubstituted alkyl group or a C_{4-8} substituted or unsubstituted cycloalkyl group, or a substituted or unsubstituted phenyl group,

Z^1 and Z^2 may be the same or different and each represents oxygen or sulphur, and

X represents hydrogen or a salt-forming

radical,
that is soluble in the water-immiscible diluent,
optionally

(iii) an organophosphinic acid or an
organothiophosphinic acid of formula



wherein

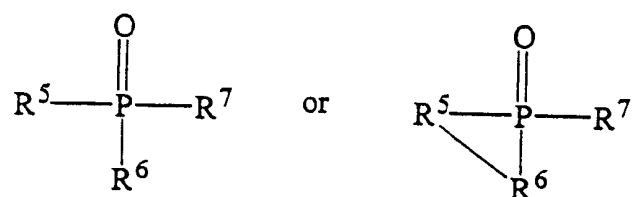
R^3 and R^4 may be the same or different and each represents a C_{4-12} substituted or unsubstituted alkyl or cycloalkyl group, or a substituted or unsubstituted phenyl group,

Z^3 and Z^4 may be the same or different and each represents oxygen or sulphur, and

X represents hydrogen or a salt-forming radical,

that is soluble in the water-immiscible diluent,

(iv) a phosphine oxide or an ester of phosphorus of formula



wherein R^5 , R^6 , and R^7 may be the same or different and each represents a C_4 - 12 substituted or unsubstituted alkyl, alkoxy, cycloalkyl, cycloalkoxy group, or a substituted or unsubstituted phenyl group, such that the number of carbons in R^5 , R^6 , and R^7 together total at least 18, and that is soluble in the water-immiscible diluent, and with the proviso that if component (ii) is the mono-2-ethylhexyl ester of mono-2-ethylhexylphosphonic acid, component (iii) is bis(2,4,4-trimethylpentyl)phosphinic acid, the sole component (iv) is tris(2,4,4-trimethylpentyl)phosphine oxide, then the amount of tris(2,4,4-trimethylpentyl)phosphine oxide is greater than 16.5%, based on the amount of bis(2,4,4-trimethylpentyl)phosphinic acid;

or

(b) contacting the lanthanide-containing extractant solution with aqueous nitric acid to transfer the lanthanide into the aqueous nitric acid, wherein the extractant solution contains the lanthanide dissolved in an extractant solvent, the solvent comprising components (i) - (iii) and optionally component (iv), with the proviso that if component (ii) is the

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mono-2-ethylhexyl ester of mono-2-ethylhexylphosphonic acid, component (iii) is bis(2,4,4-trimethylpentyl)phosphinic acid, then tris(2,4,4-trimethylpentyl)phosphine oxide is absent or is present in an amount not greater than 13.8%, based on the amount of bis(2,4,4-trimethylpentyl)phosphinic acid.

2. A process according to claim 1, wherein about 0.5 to 4M aqueous hydrochloric acid is used to strip in step (a).

3. A process according to claim 2, wherein the concentration of aqueous hydrochloric acid is about 1 to 2M.

4. A process according to claim 1, wherein about 0.5 to 4M aqueous nitric acid is used to strip in step (b).

5. A process according to claim 4, wherein the concentration of aqueous nitric acid is about 1 to 2.5M.

6. A process according to any one of claims 1 to 5 wherein component (ii) is present in the extractant solvent in an amount of about 0.1 to about 1M.

7. A process according to any one of claims 1 to 6, wherein component (iii) is present in the extractant solvent in an amount of about 0.1 to about 1M.

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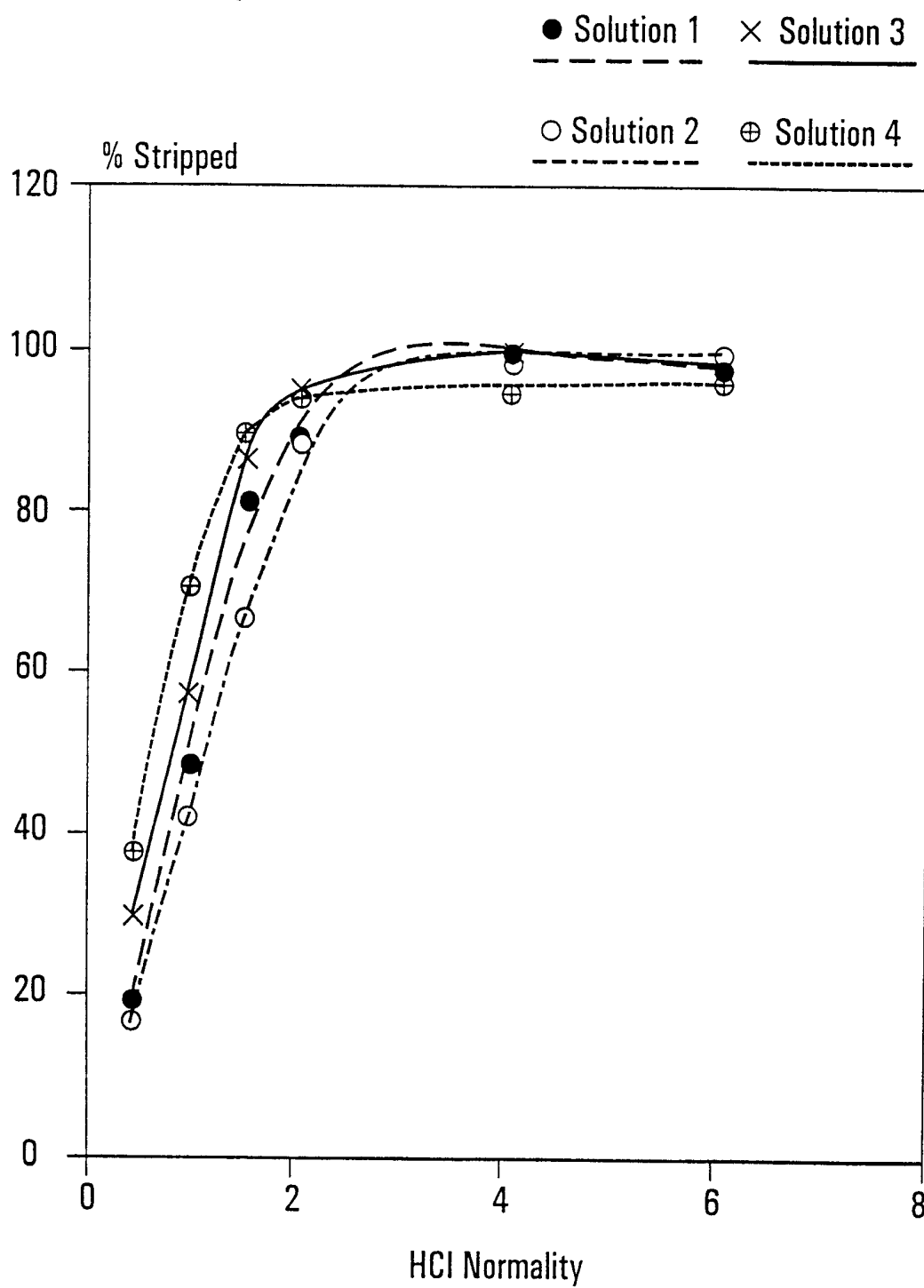
8. A process according to any one of claims 1 to 7, wherein the lanthanide is present in the extractant solution in an amount of about 0.005 to about 0.2M.
9. A process according to any one of claims 1 to 8, wherein component (iv) is present in an amount of about 0.05 to 0.6M in step (a).
10. A process according to any one of claims 1 to 8, wherein component (iv) is present in an amount of 0 to 0.1M in step (b).
11. A process according to any one of claims 1 to 10, wherein Z^1 and Z^2 both represent oxygen.
12. A process according to any one of claims 1 to 11, wherein Z^3 and Z^4 both represent oxygen.
13. A process according to any one of claims 1 to 12, wherein component (iv) is a phosphine oxide.
14. A process according to any one of claims 1 to 13 wherein the lanthanide-containing extractant solution is obtained by subjecting an aqueous acidic leachate of a lanthanide-containing ore to extraction with an extractant solution as defined in step (a) or in step (b) of claim 1.

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15. A process according to any one of claims 1 to 14 which comprises the step of precipitating a lanthanide from the aqueous hydrochloric or nitric acid.

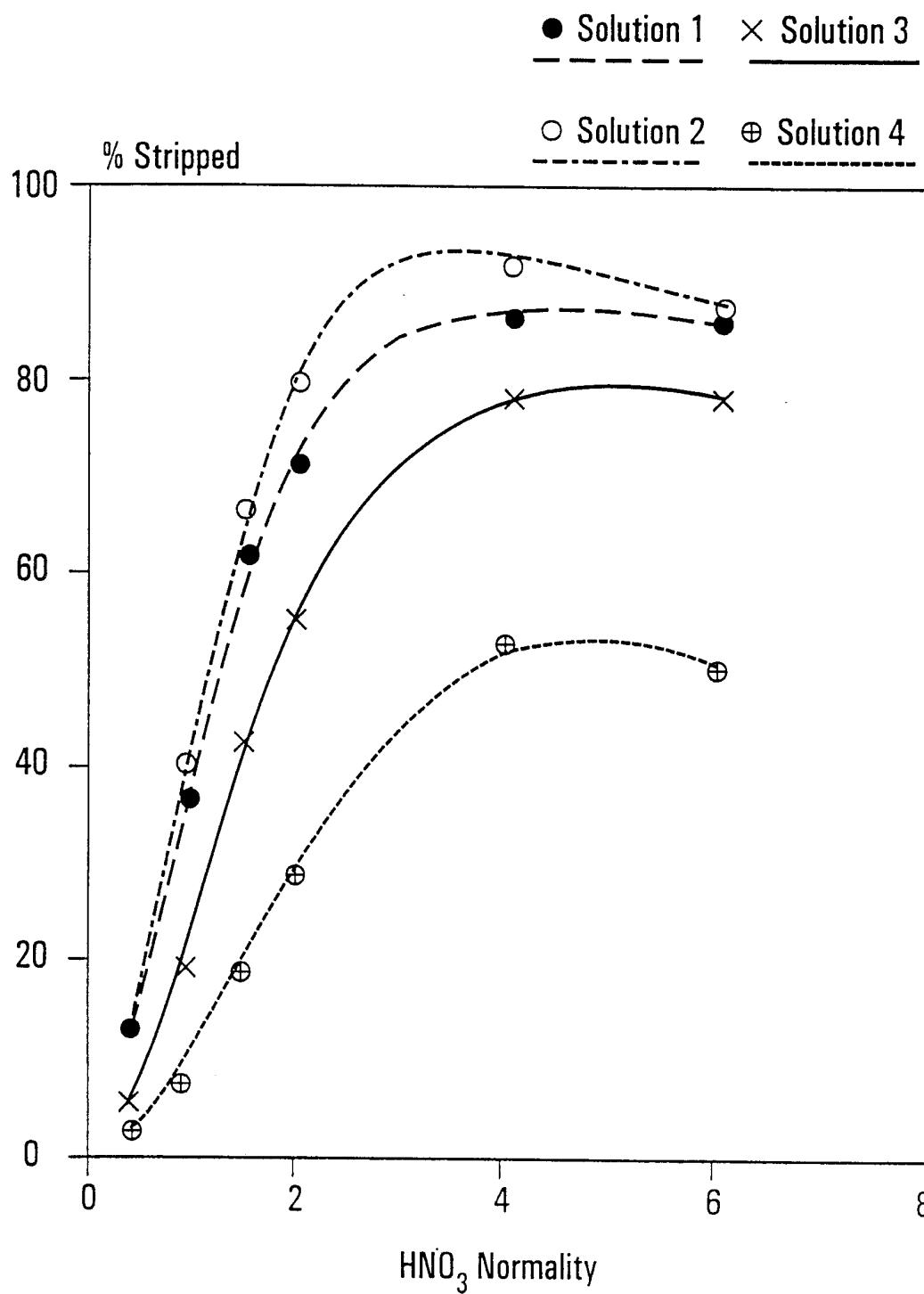
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FIG. 1

Effect of $R_3P(O)$ on Yb Stripping with Hydrochloric Acid

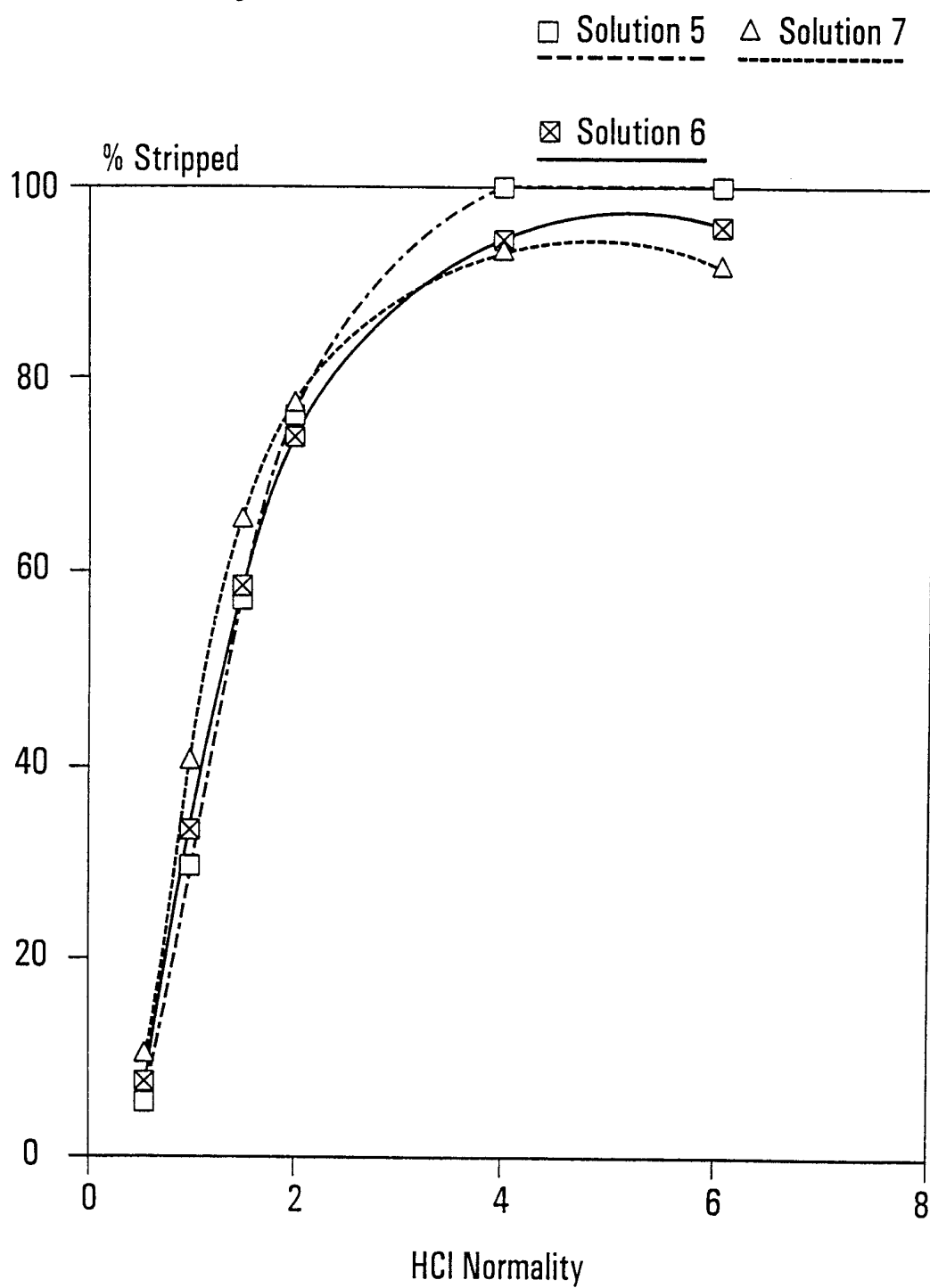
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FIG. 2

Effect of $R_3P(O)$ on Yb Stripping with Nitric Acid

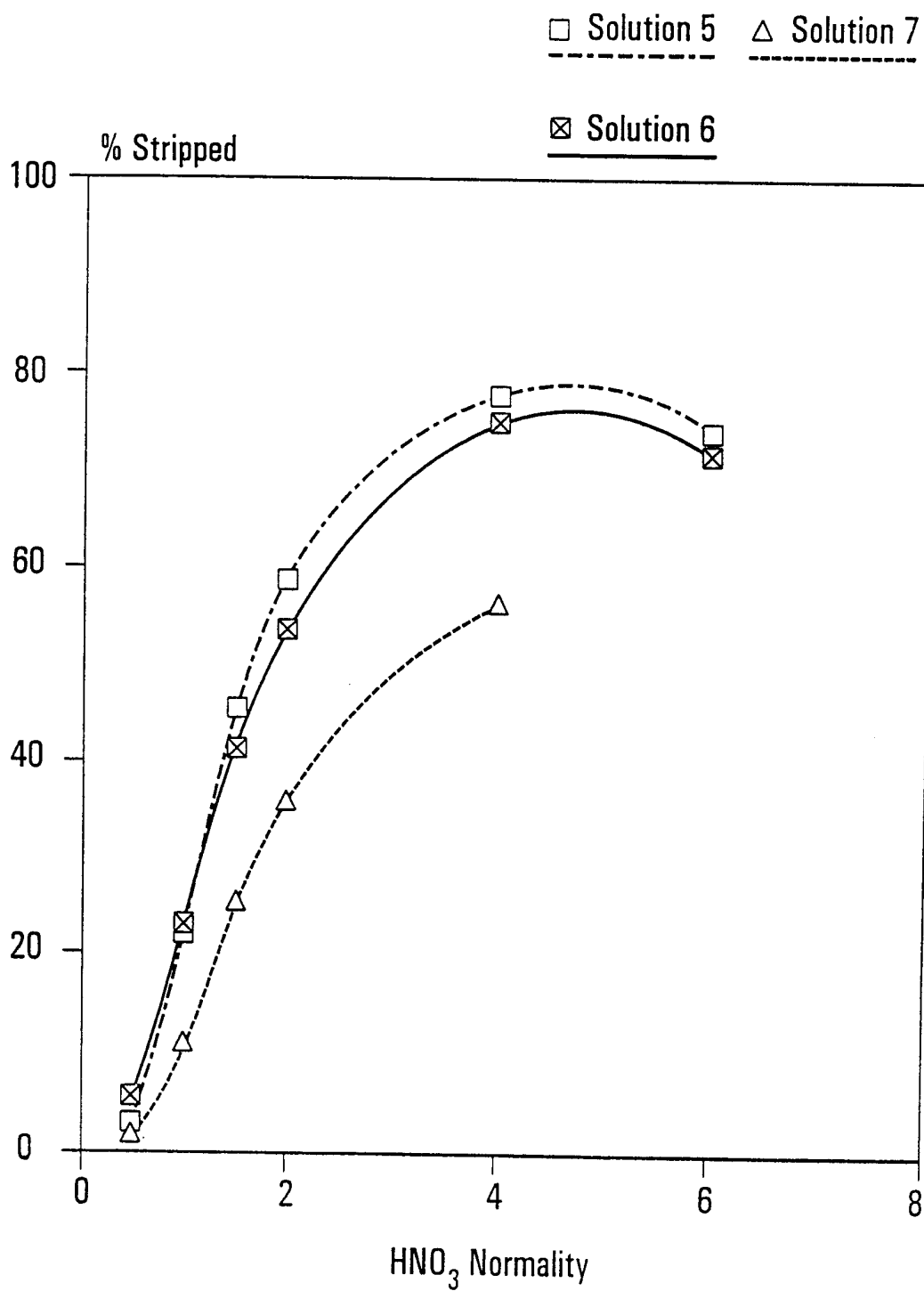
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FIG. 3

Effect of $R_3P(O)$ on Yb Stripping with Hydrochloric Acid

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FIG. 4

Effect of $R_3P(O)$ on Yb Stripping with Nitric Acid

INTERNATIONAL SEARCH REPORT

Internal Application No

PCT/US 00/18359

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C22B3/38 C22B59/00 C22B3/40

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)

IPC 7 C22B

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 practical, search terms used)

EPO-Internal, WPI Data, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5 639 433 A (YUAN CHENGYE ET AL) 17 June 1997 (1997-06-17) cited in the application the whole document ----	1-15
Y	US 5 015 447 A (FULFORD GEORGE D ET AL) 14 May 1991 (1991-05-14) column 2; claim 5; examples 3,4; tables 2-4 ----	1-15
Y	US 4 461 747 A (FITOUSSI RICHARD ET AL) 24 July 1984 (1984-07-24) claims 1-5; example 2 ----	1-15
Y	EP 0 233 121 A (RHONE POULENC CHIMIE) 19 August 1987 (1987-08-19) claims 3,4,7,9-13,20-22; examples 1,2,4 ----- -/-	1-3,8, 11-15

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

11 October 2000

Date of mailing of the international search report

18/10/2000

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 00/18359

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 647 438 A (SABOT JEAN-LOUIS ET AL) 3 March 1987 (1987-03-03) claims 1-8,14-16; examples 1-4 -----	1,4,5,7, 13-15

INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No

PCT/US 00/18359

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5639433 A	17-06-1997	AU 713206 B JP 9176757 A BR 9605956 A	25-11-1999 08-07-1997 18-08-1998
US 5015447 A	14-05-1991	AU 624300 B AU 5884290 A BR 9003451 A CA 2021415 A	04-06-1992 24-01-1991 27-08-1991 19-01-1991
US 4461747 A	24-07-1984	NONE	
EP 0233121 A	19-08-1987	FR 2594429 A AT 58398 T AU 593061 B AU 6878687 A BR 8700668 A DE 3766119 D JP 62253739 A	21-08-1987 15-11-1990 01-02-1990 20-08-1987 15-12-1987 20-12-1990 05-11-1987
US 4647438 A	03-03-1987	FR 2562059 A AT 36008 T AU 569212 B AU 4055385 A BR 8501508 A CA 1233025 A DE 3563983 D EP 0156735 A FI 851303 A,B, GB 2156795 A,B JP 1662022 C JP 3029006 B JP 60251126 A KR 9108928 B NO 851284 A,B, ZA 8502441 A	04-10-1985 15-08-1988 21-01-1988 09-10-1986 26-11-1985 23-02-1988 01-09-1988 02-10-1985 03-10-1985 16-10-1985 19-05-1992 22-04-1991 11-12-1985 26-10-1991 03-10-1985 27-11-1985