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Boudreault et al.(10) **Pub. No.: US 2015/0104361 A1**(43) **Pub. Date: Apr. 16, 2015**(54) **PROCESSES FOR RECOVERING RARE
EARTH ELEMENTS AND RARE METALS**(71) Applicant: **ORBITE ALUMINAE INC.**,
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Marie-Maxime Labrecque-Gilbert,
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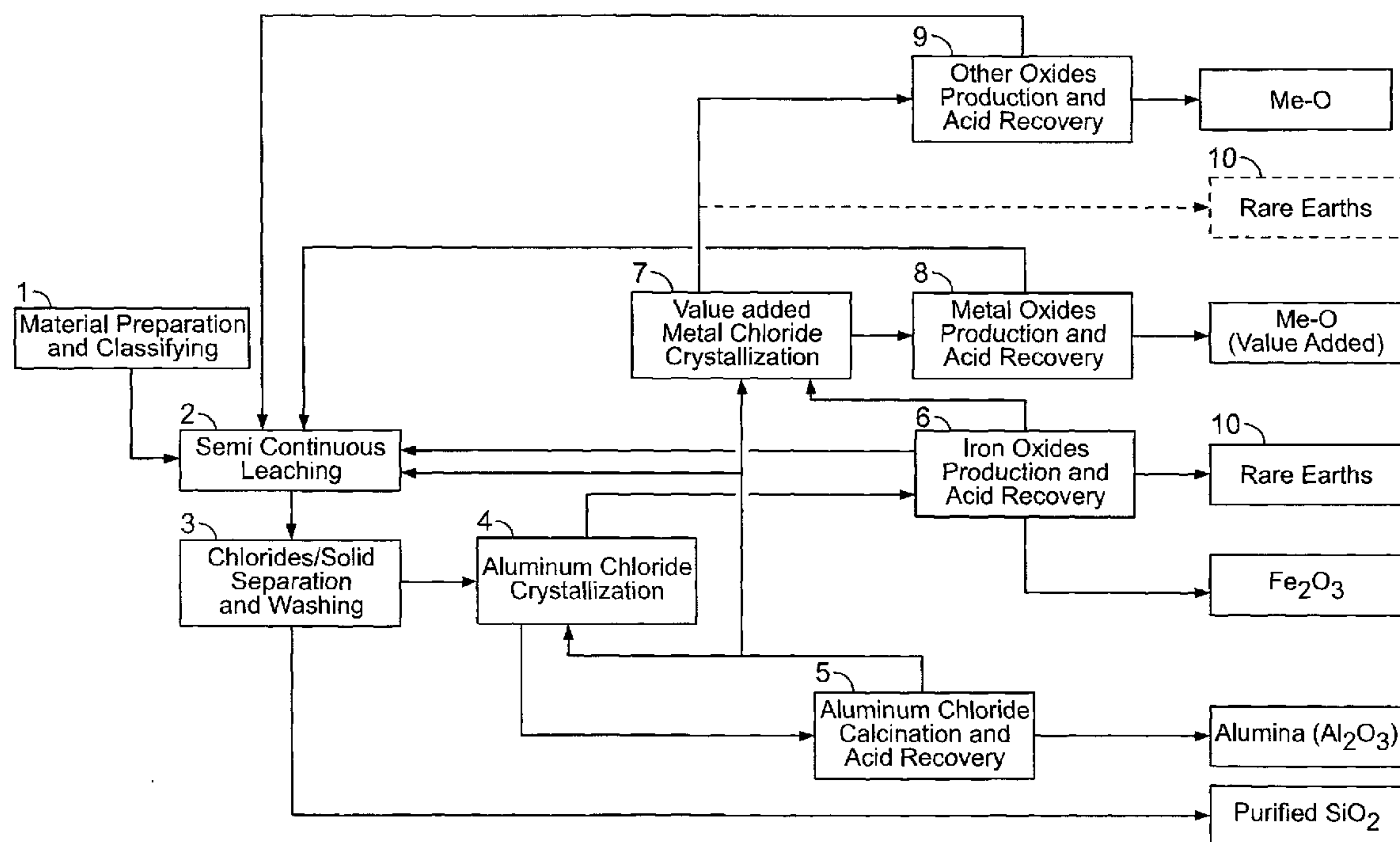
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19, 2012, provisional application No. 61/705,807,
filed on Sep. 26, 2012.(30) **Foreign Application Priority Data**

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C22B 59/00 (2006.01)(52) **U.S. Cl.**
CPC **C22B 59/00** (2013.01)(57) **ABSTRACT**

There are provided processes for recovering at least one rare earth element. Such processes comprise obtaining an acidic composition comprising (i) at least one rare earth element and optionally at least one rare metal; and reacting the composition with a precipitating agent so as to substantially selectively precipitate a first rare earth element and optionally a first rare metal. For example, various rare earth elements (such as scandium, yttrium, lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, etc) and various rare metals (such as indium, zirconium, lithium, gallium, etc.) can be extracted by using such processes.



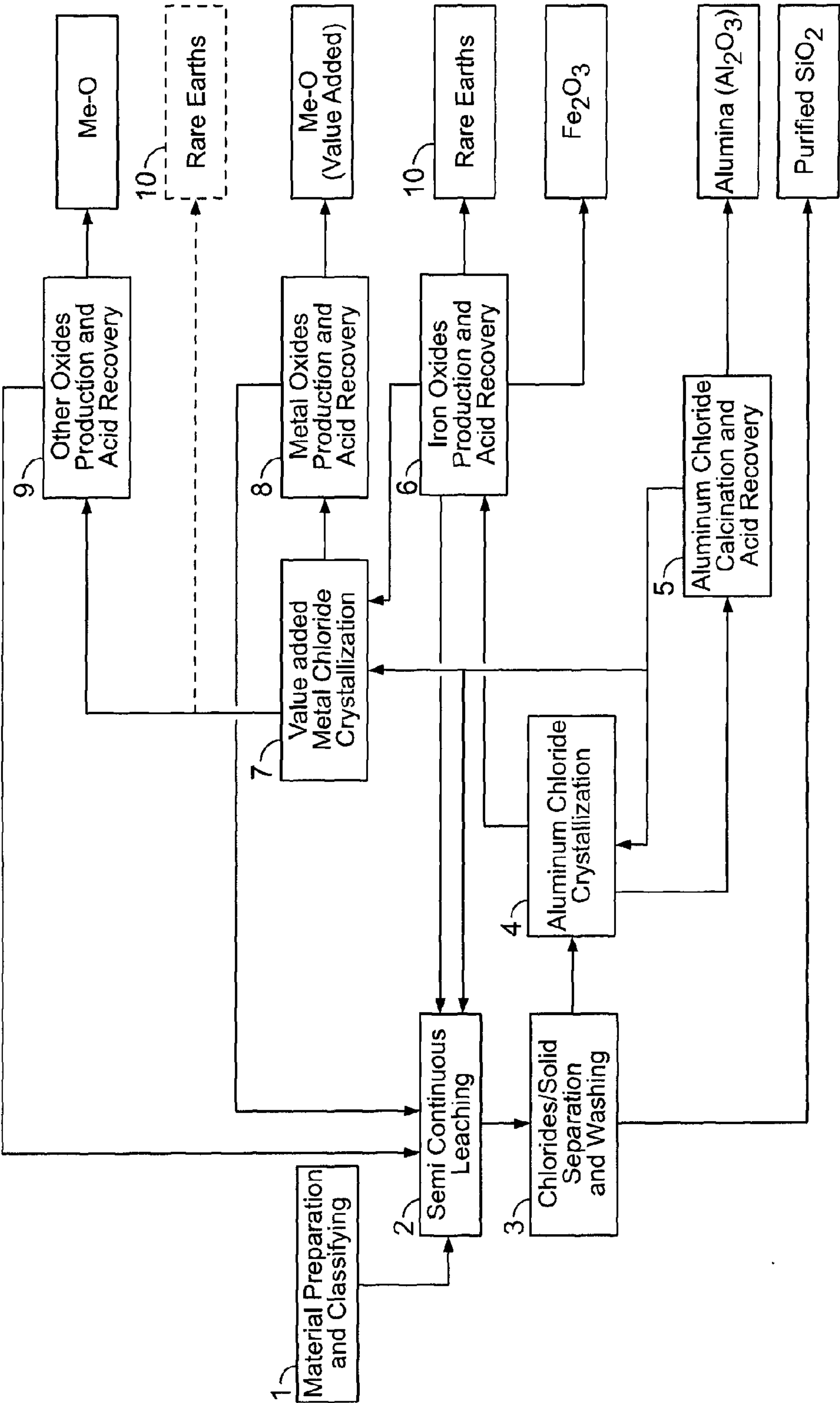


FIG. 1

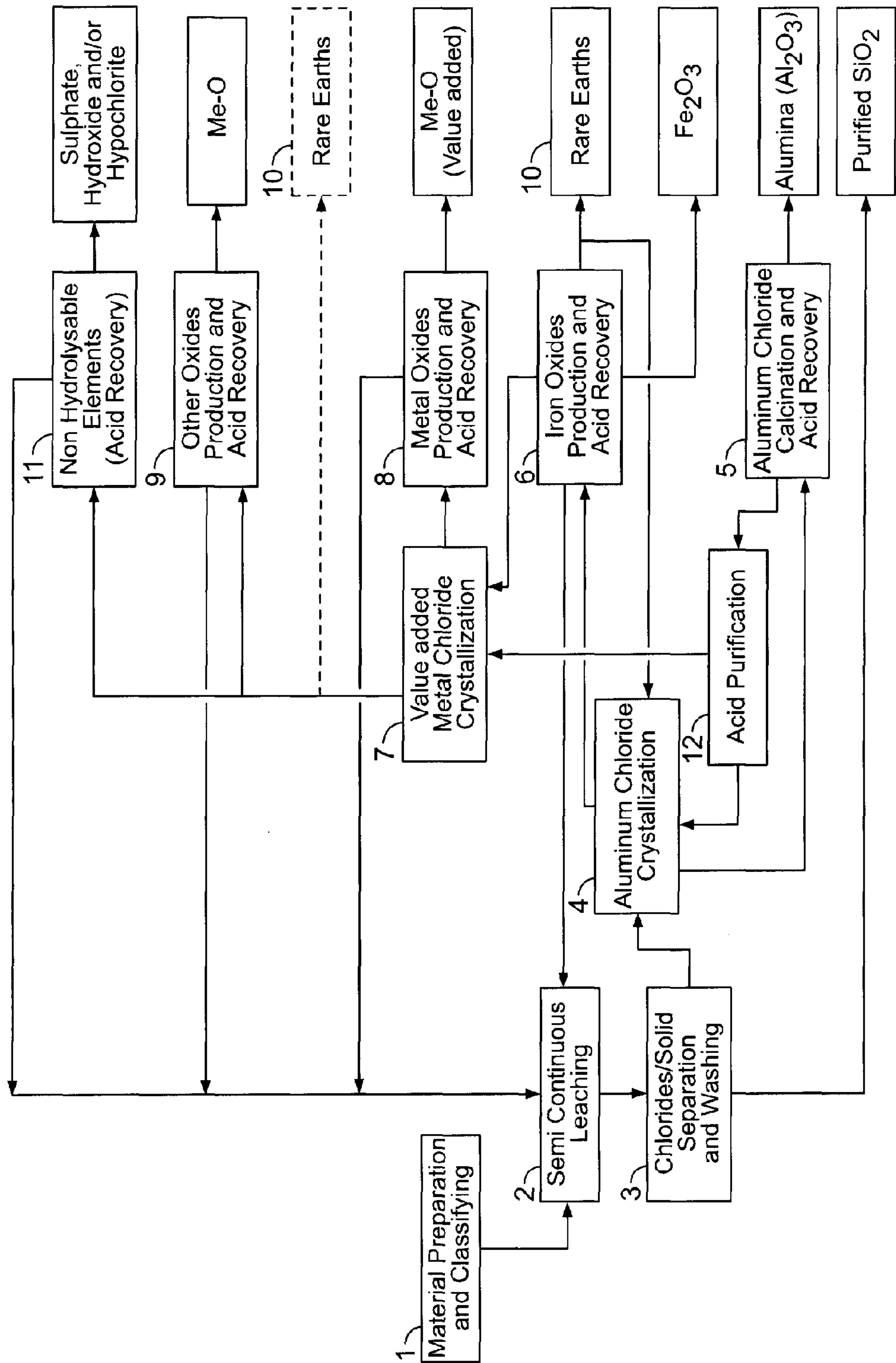


FIG. 2

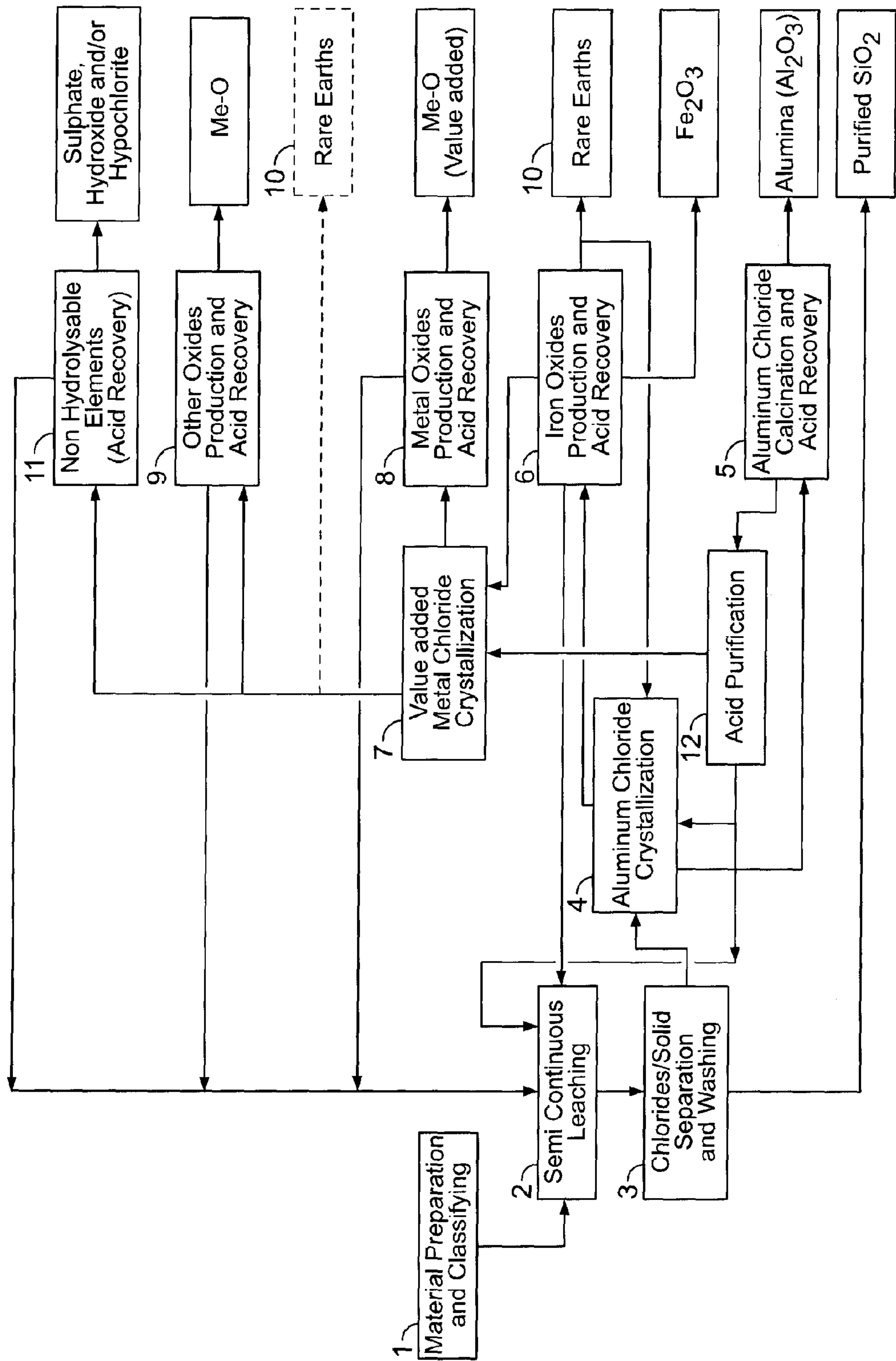


FIG. 2A

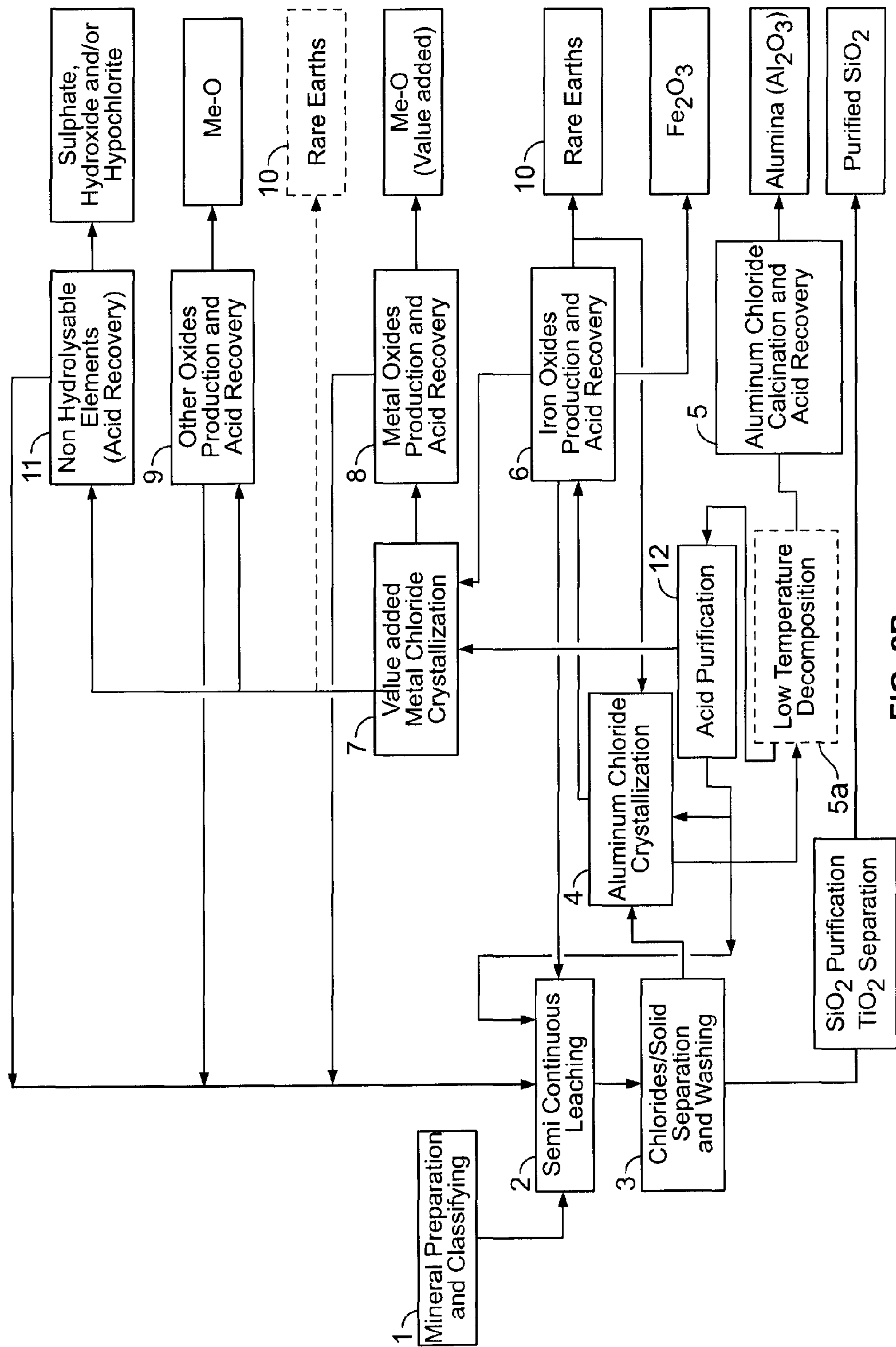


FIG. 2B

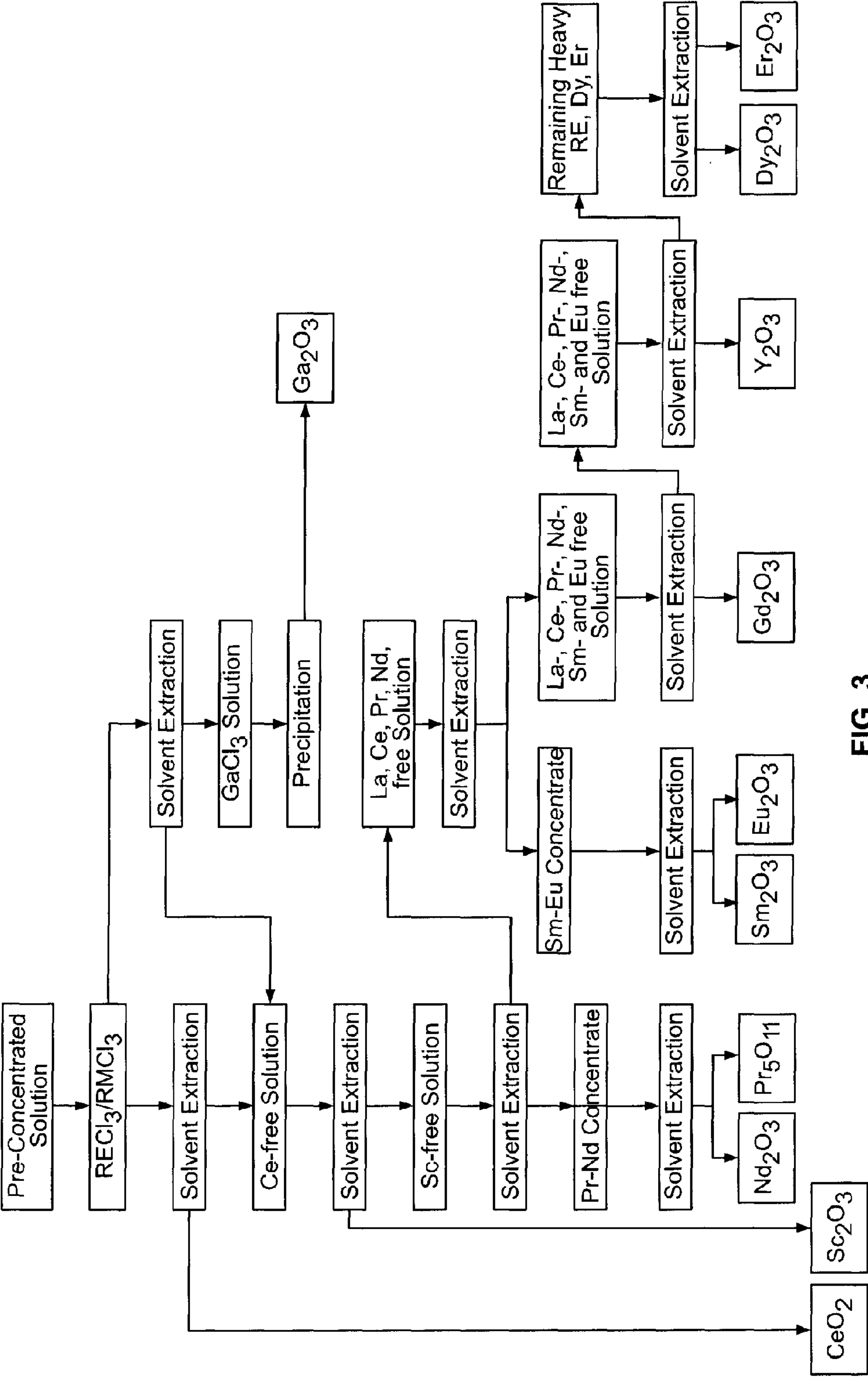


FIG. 3

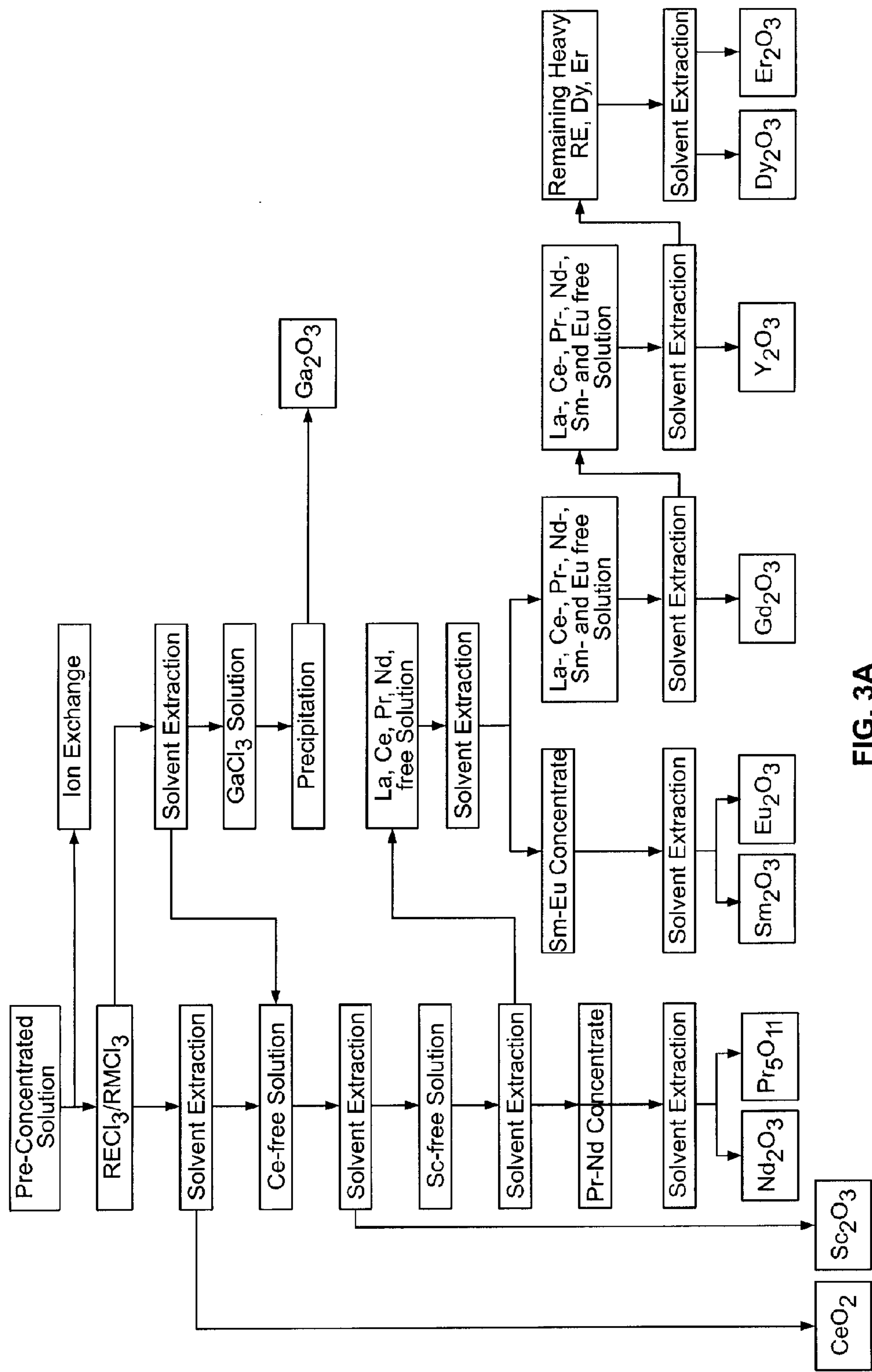


FIG. 3A

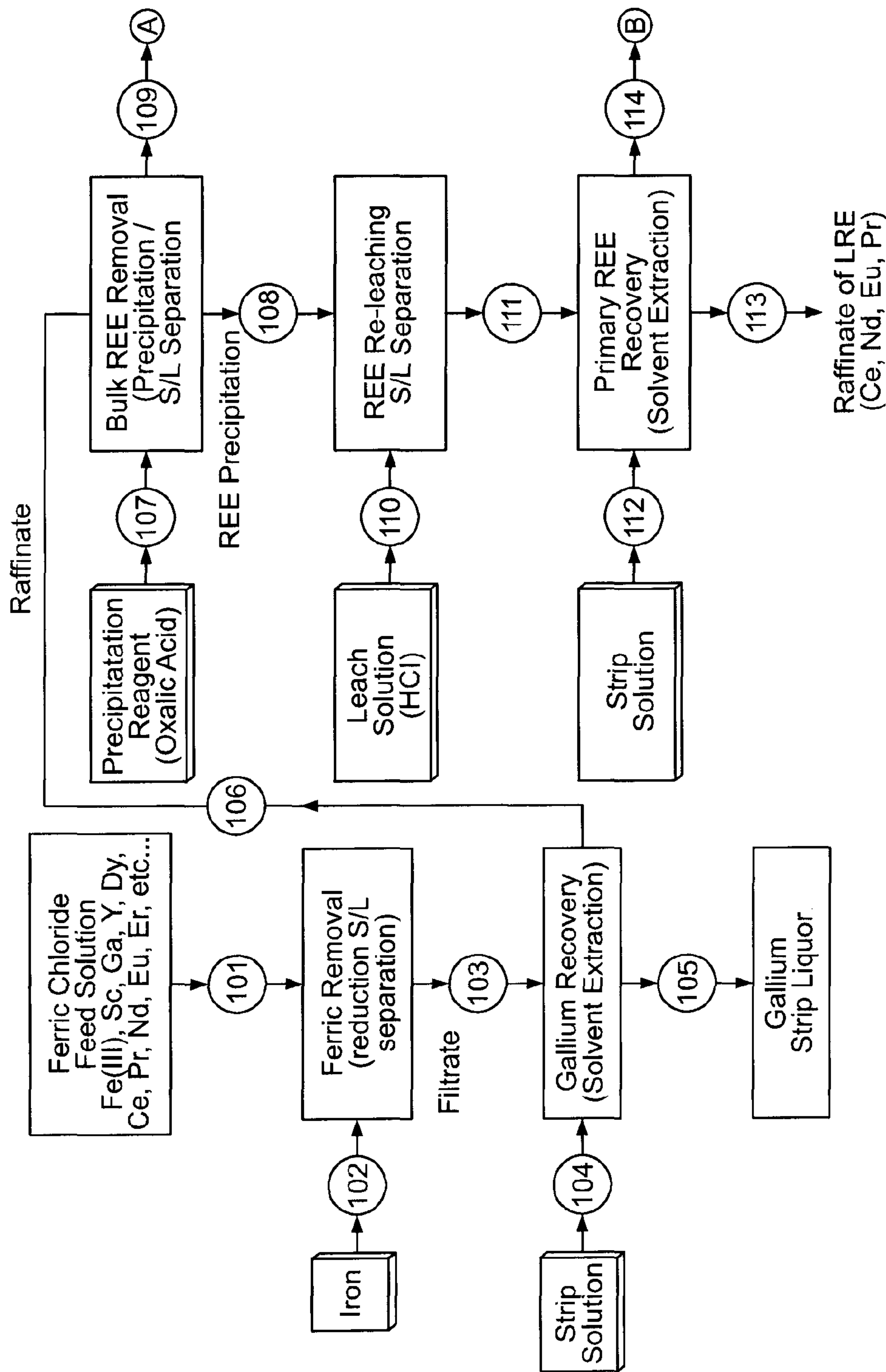


FIG. 4A

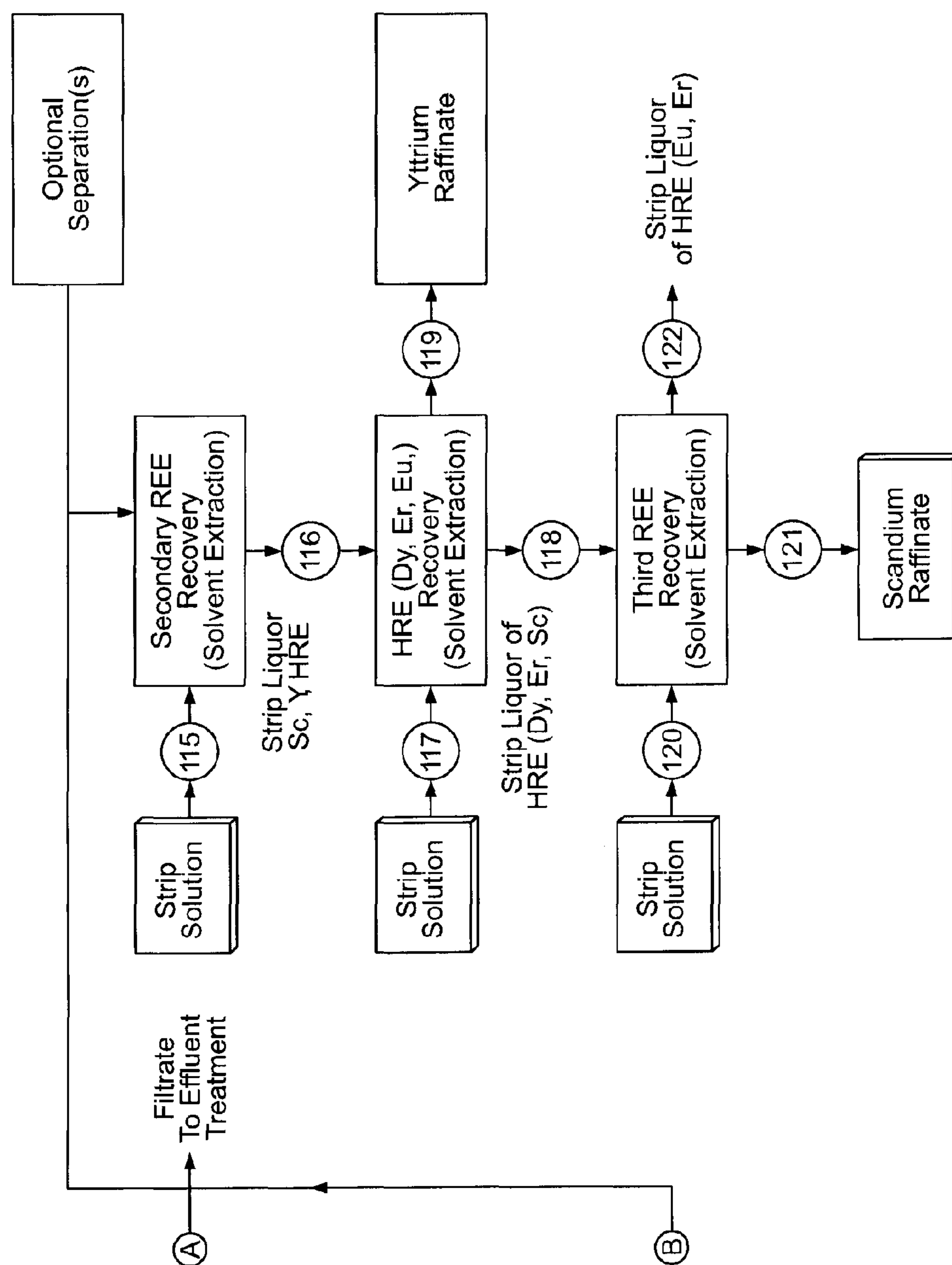


FIG. 4B

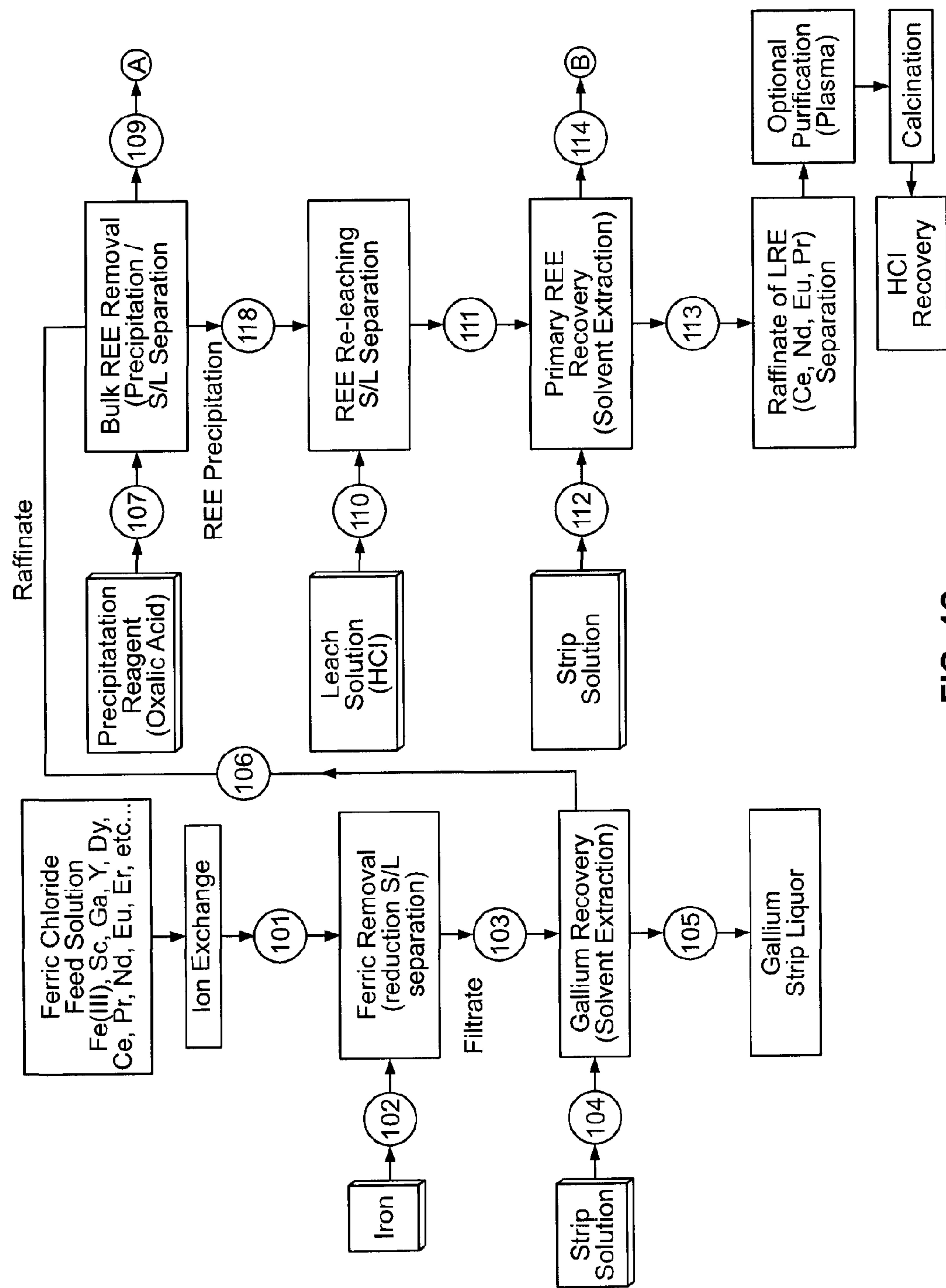


FIG. 4C

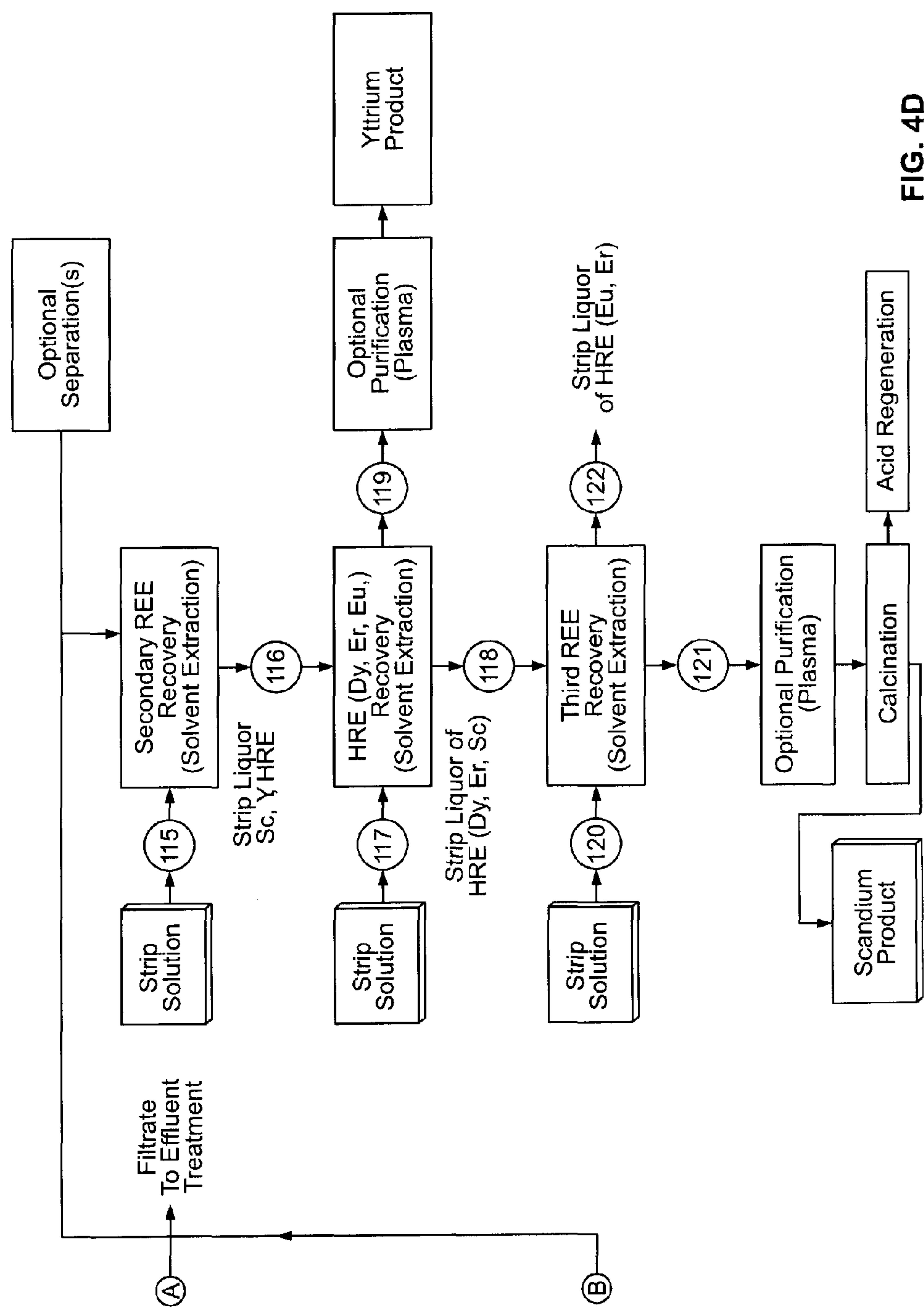
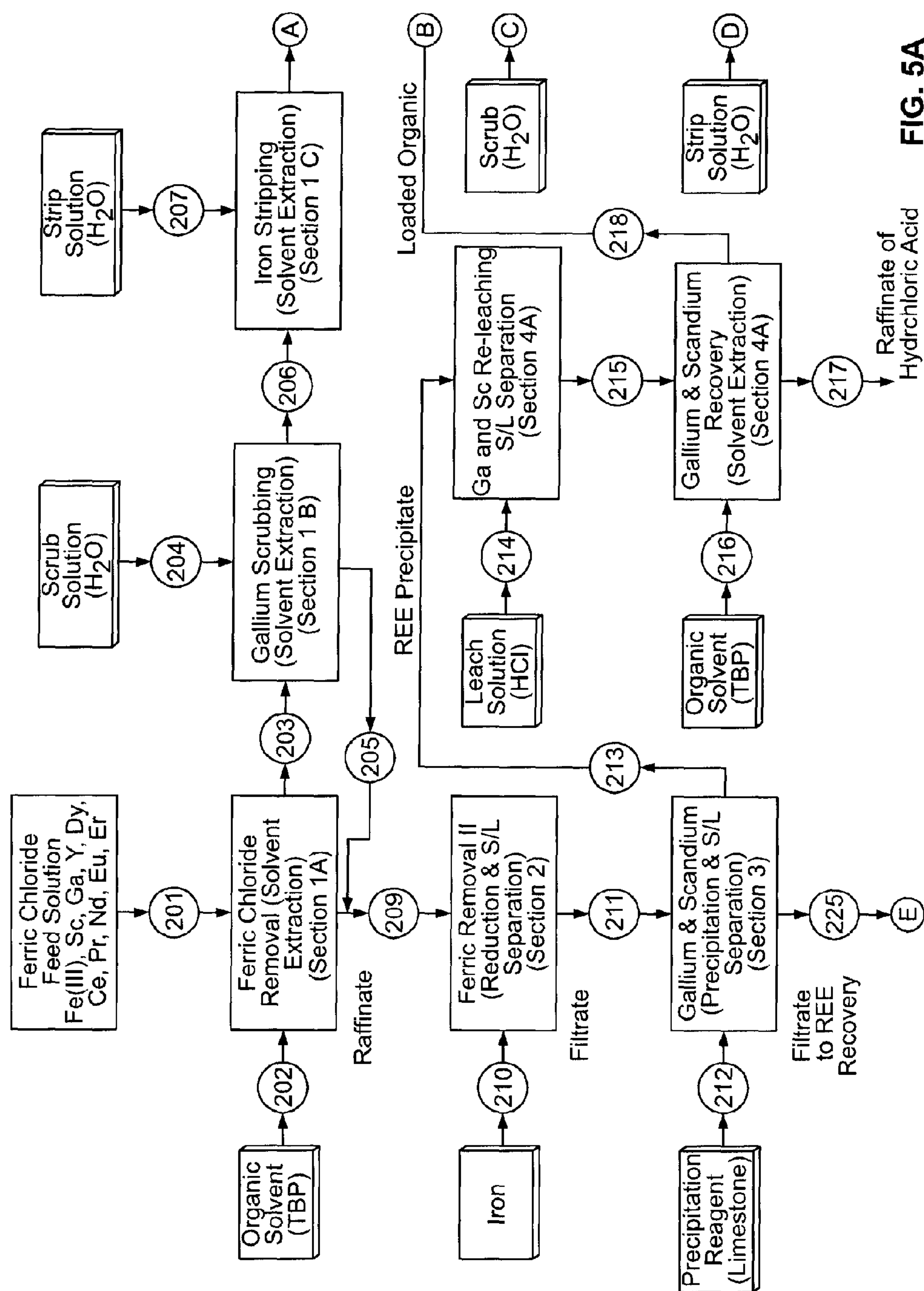


FIG. 4D



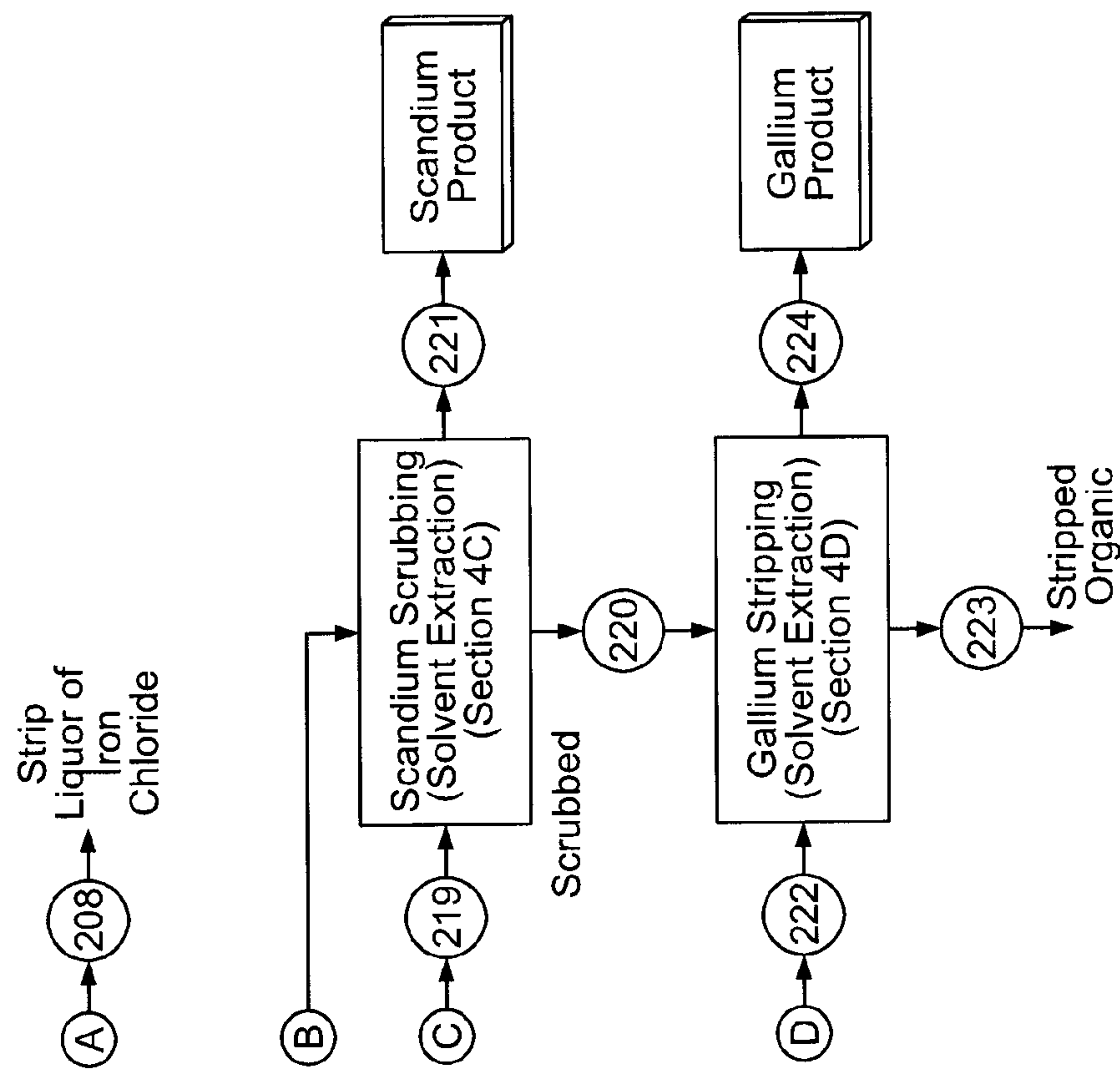


FIG. 5B

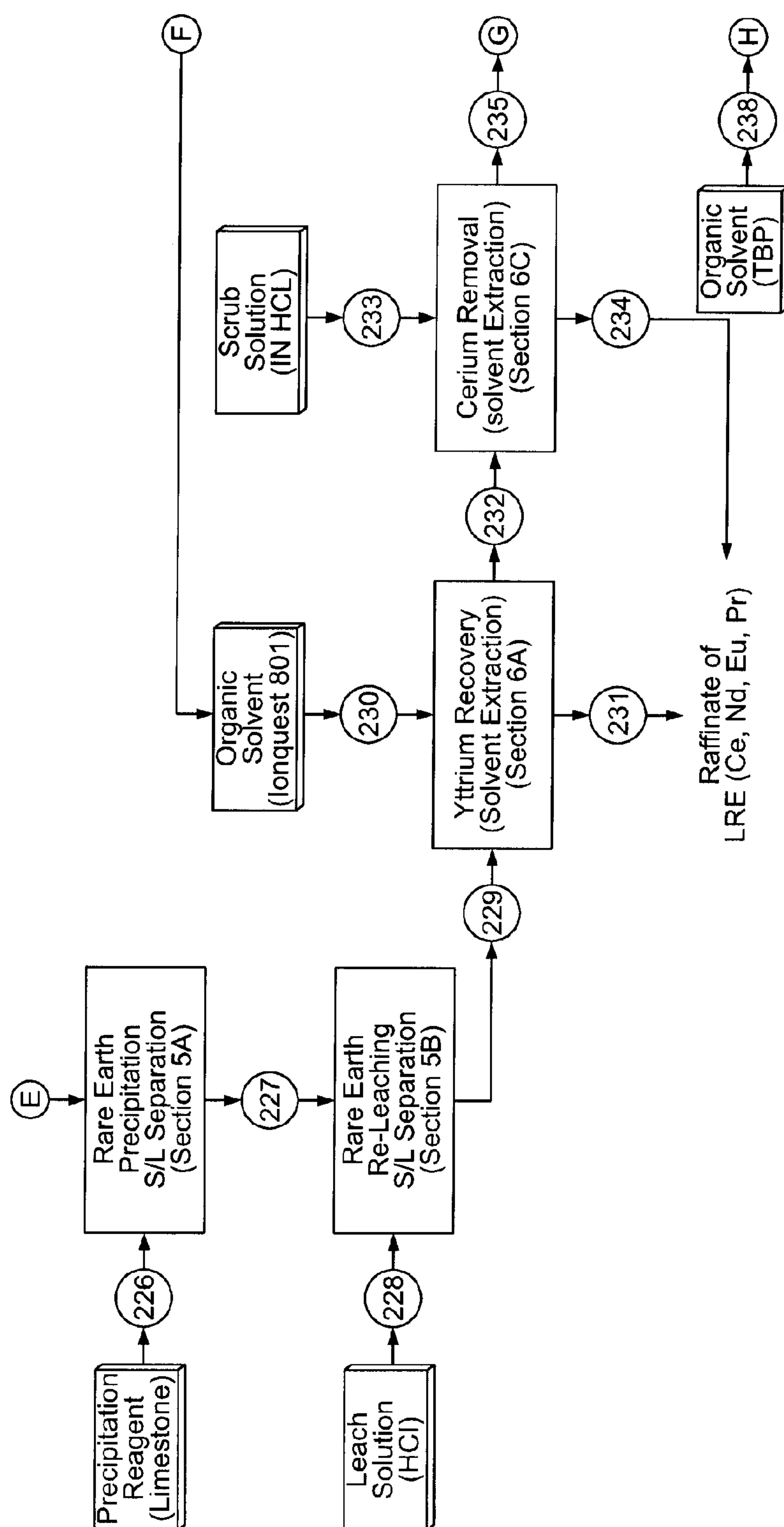


FIG. 5C

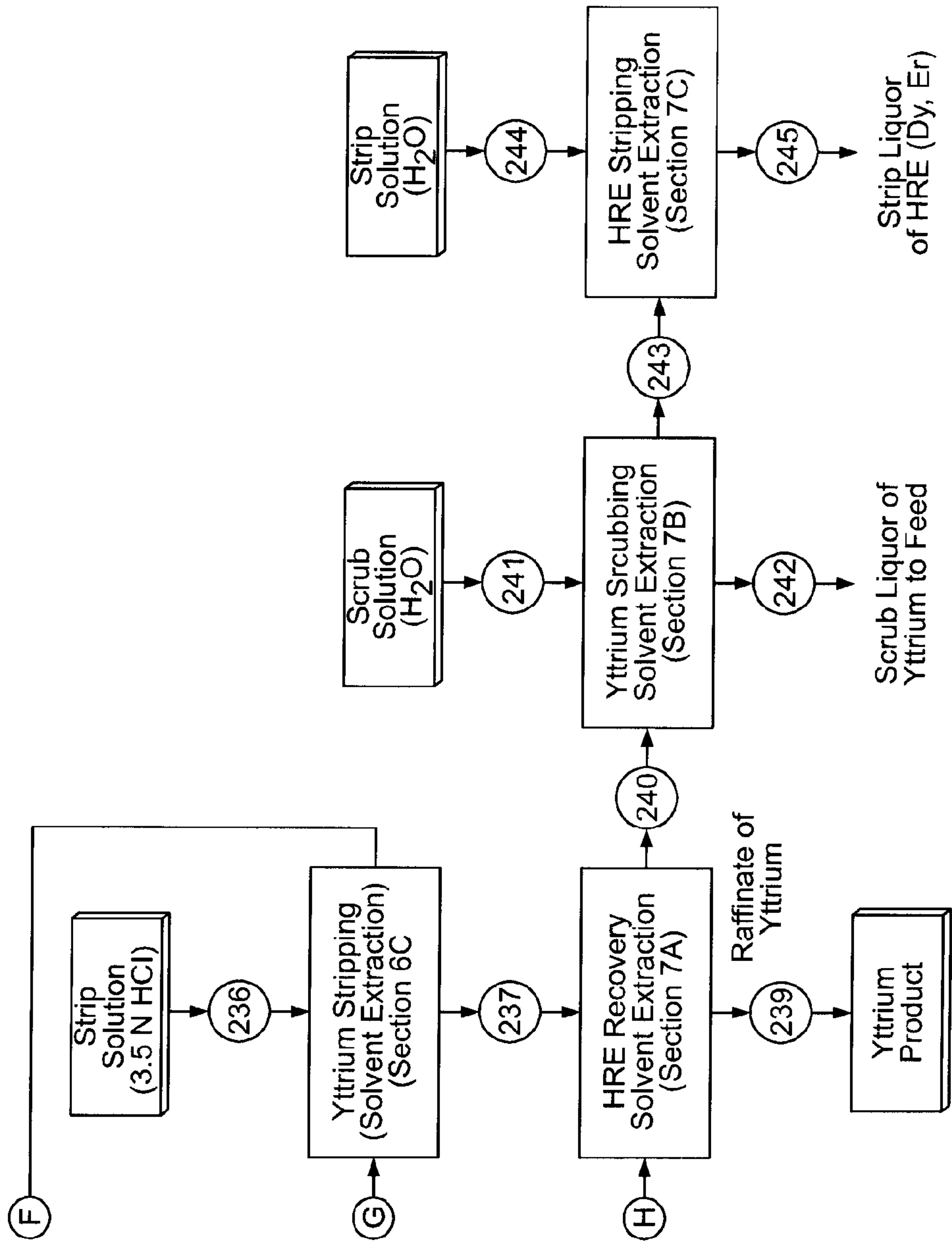


FIG. 5D

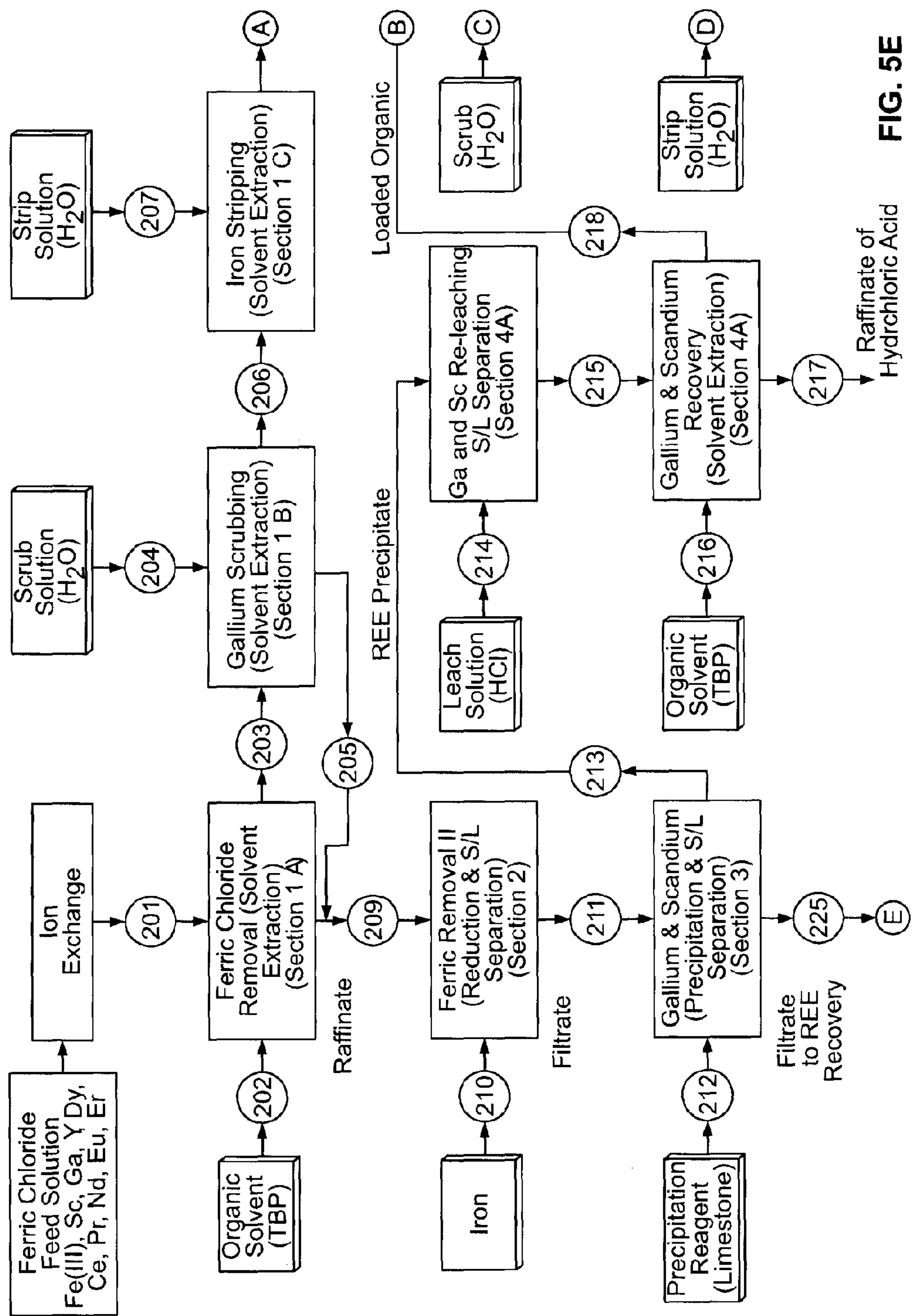


FIG. 5E

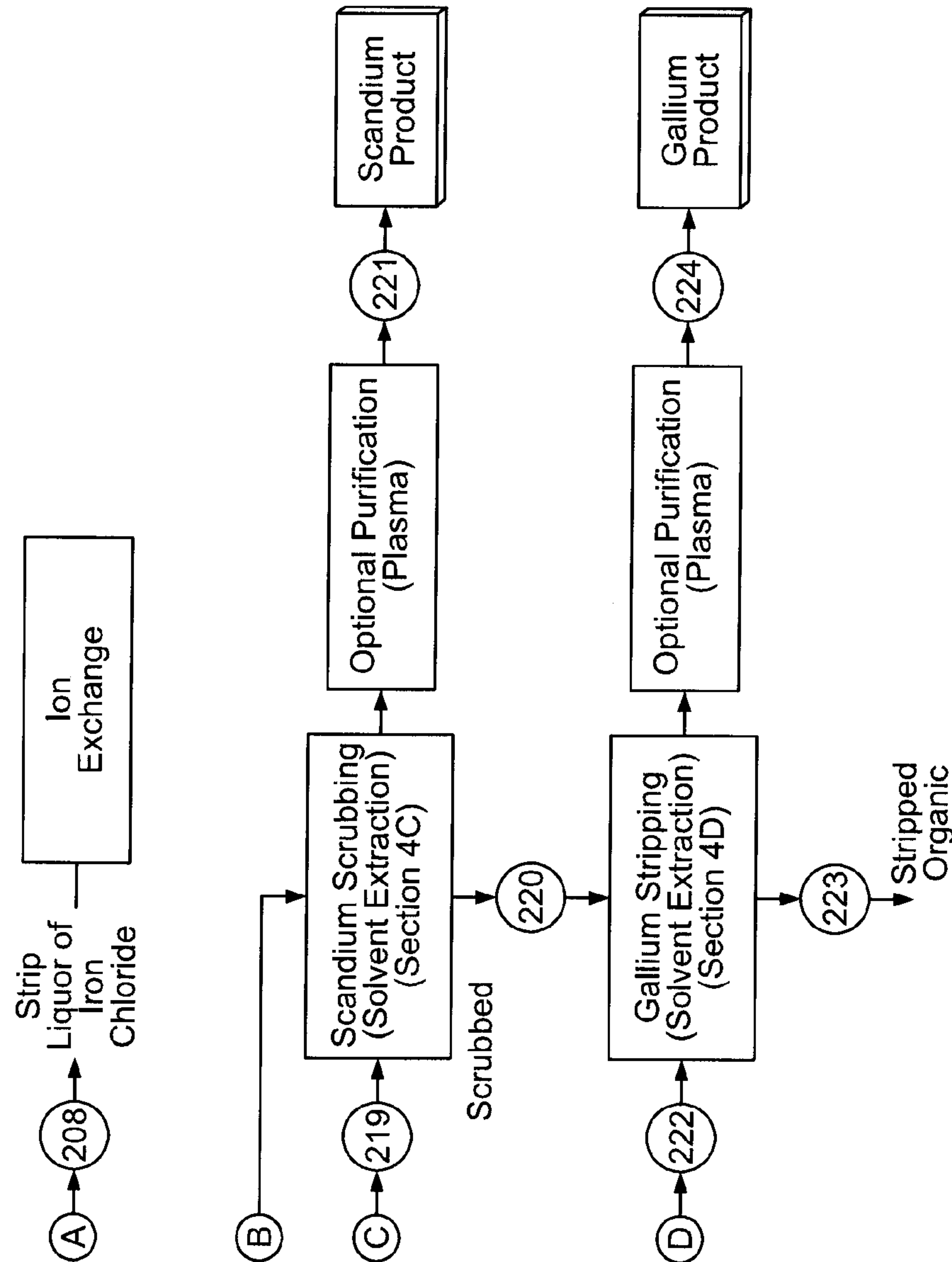
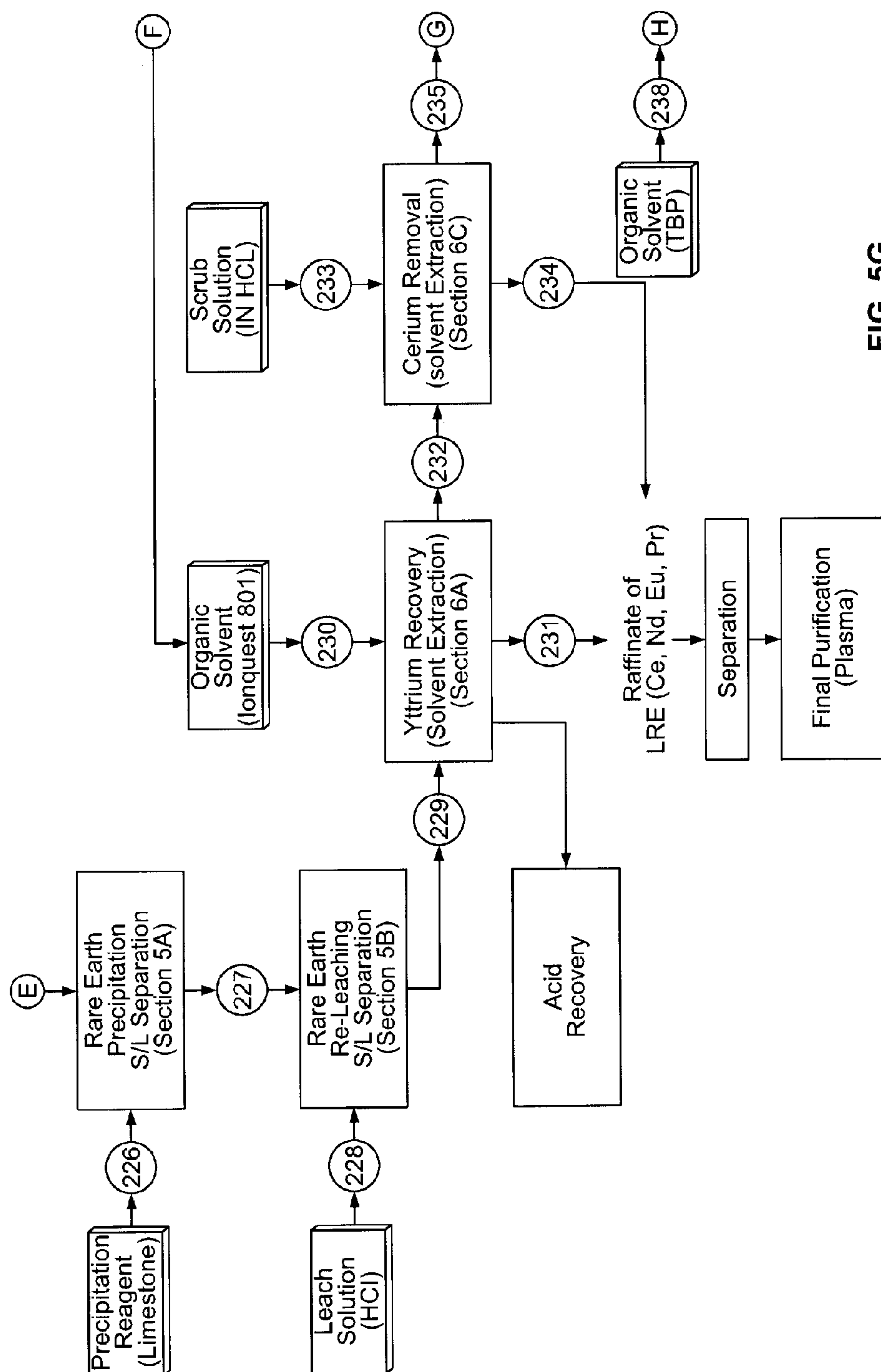


FIG. 5F



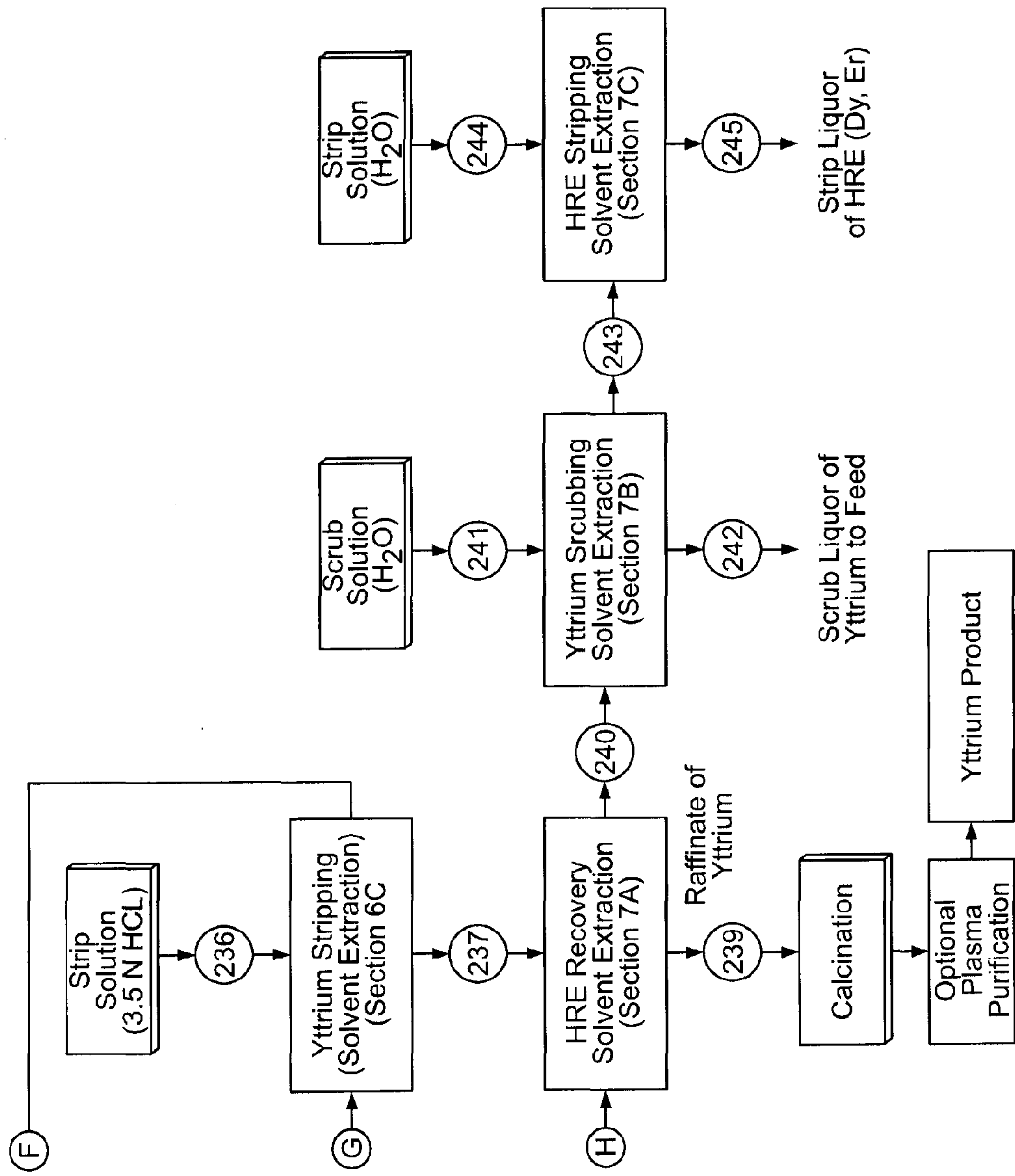


FIG. 5H

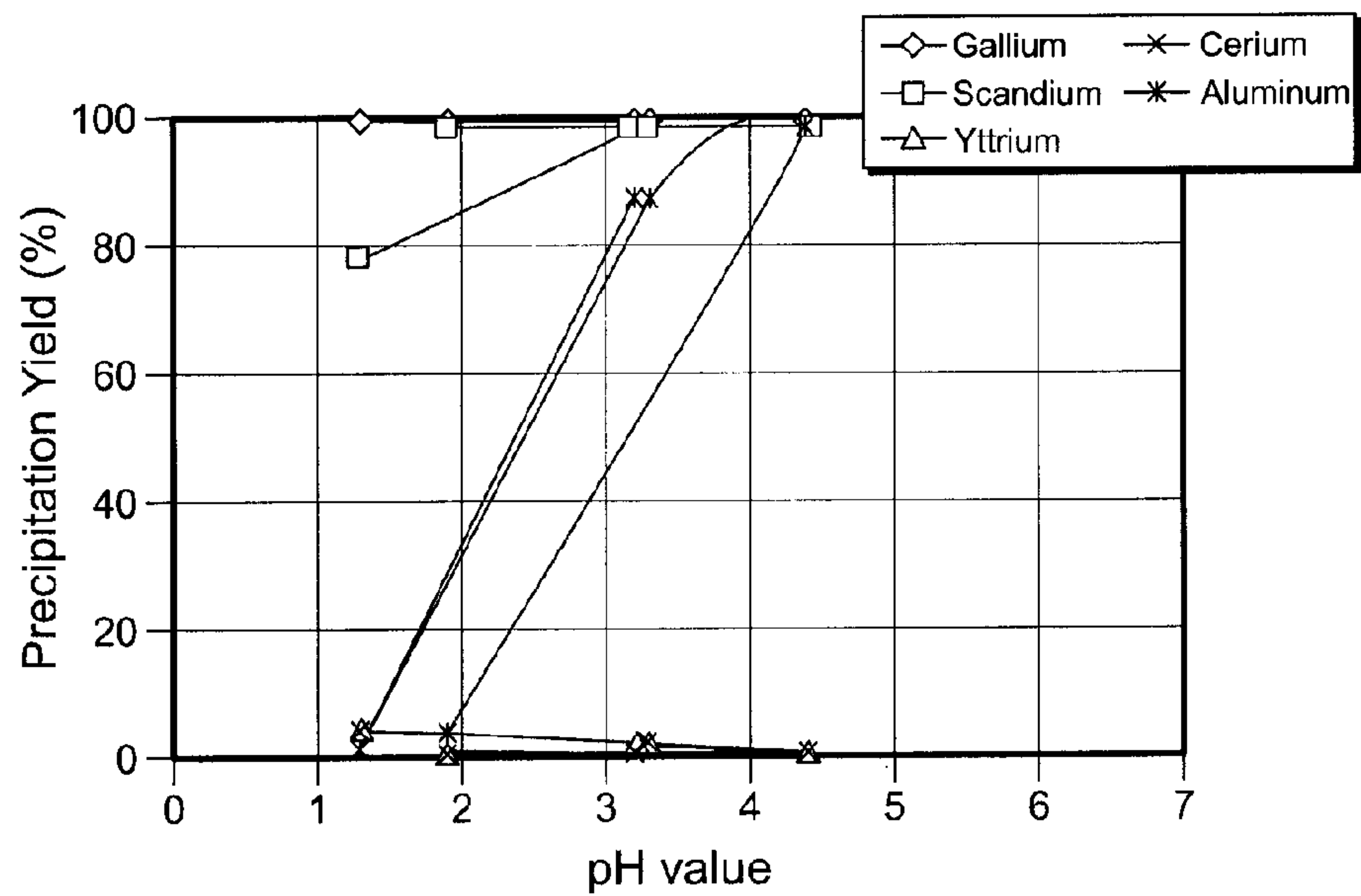


FIG. 6

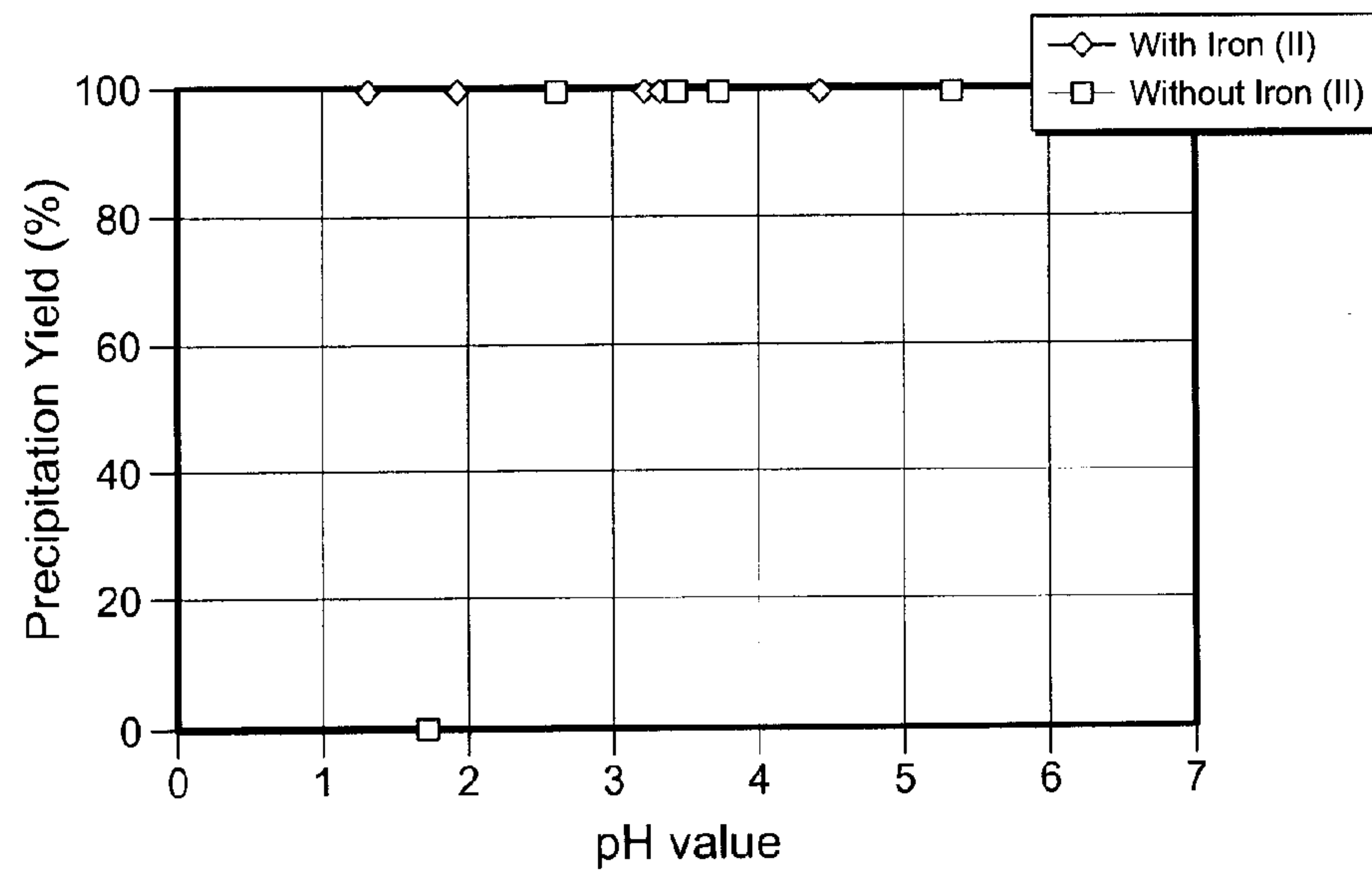


FIG. 7

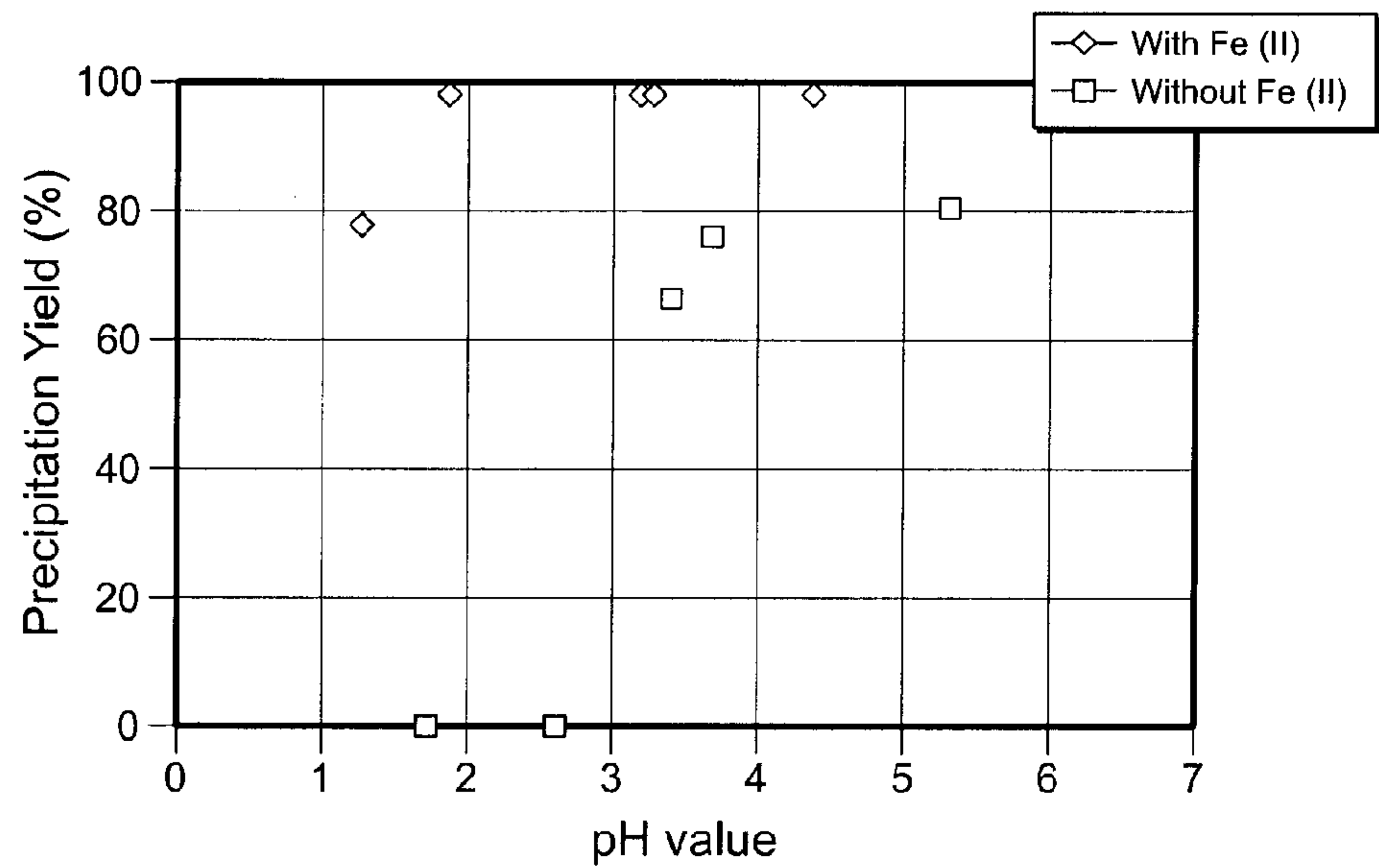


FIG. 8

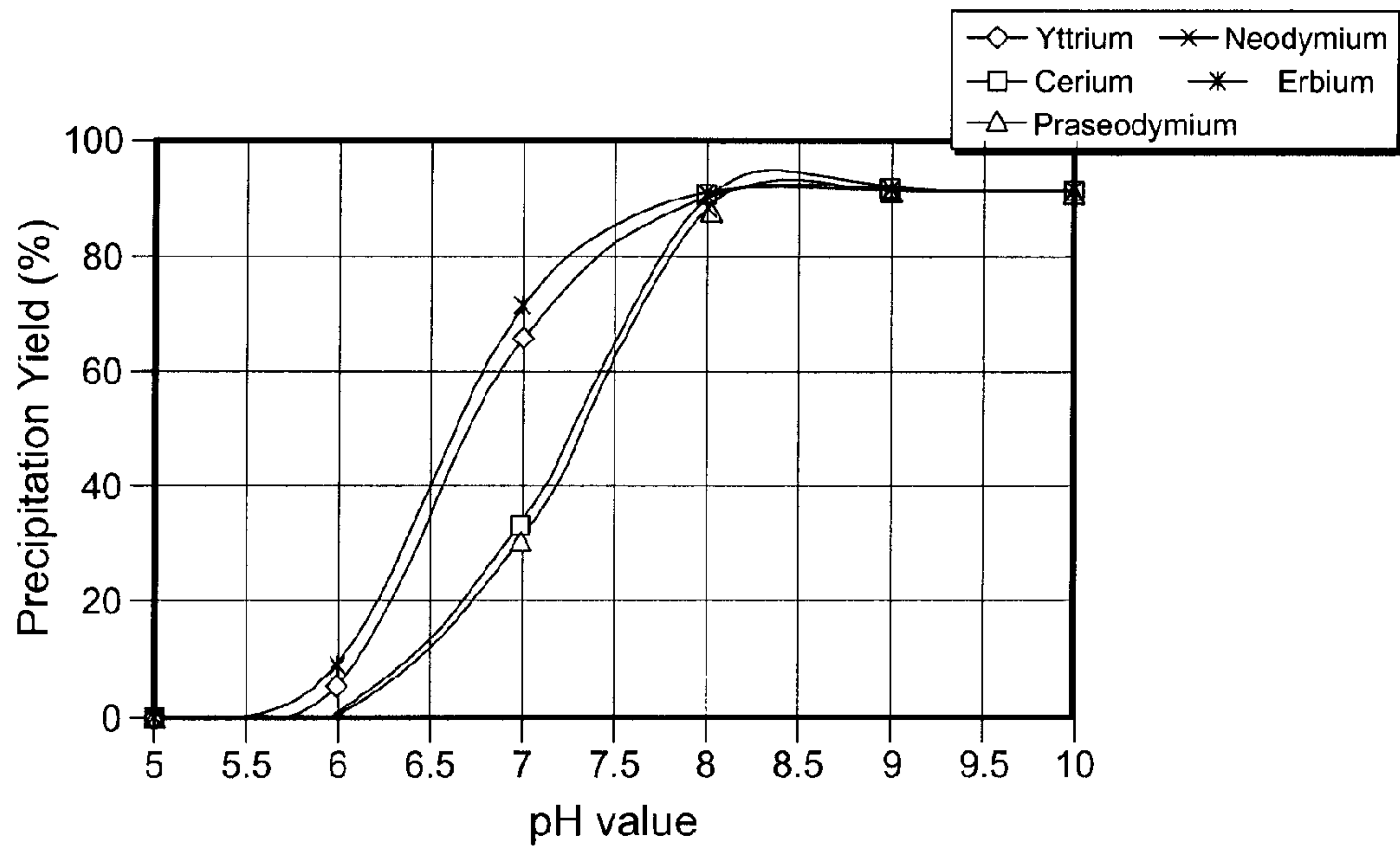


FIG. 9

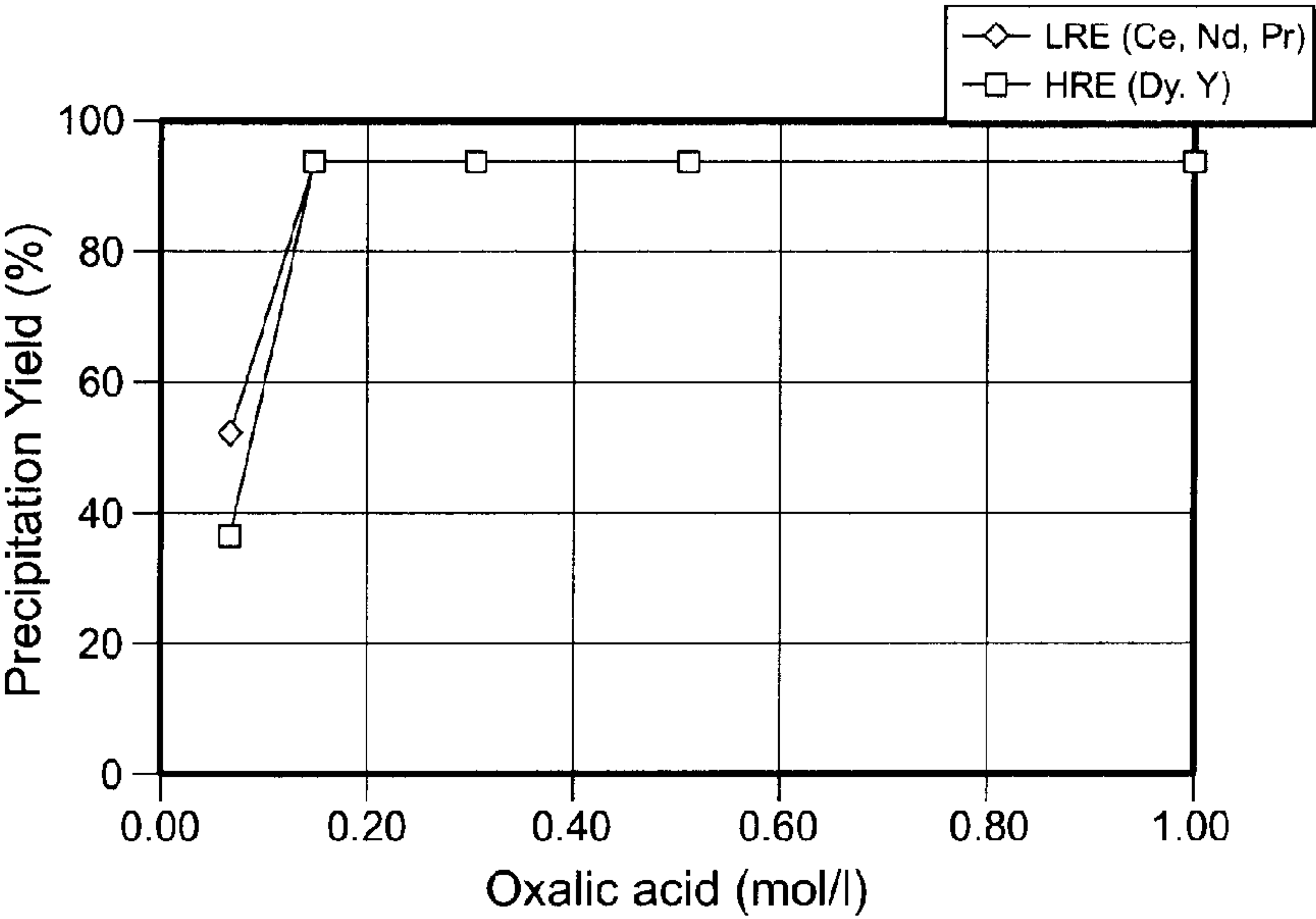


FIG. 10

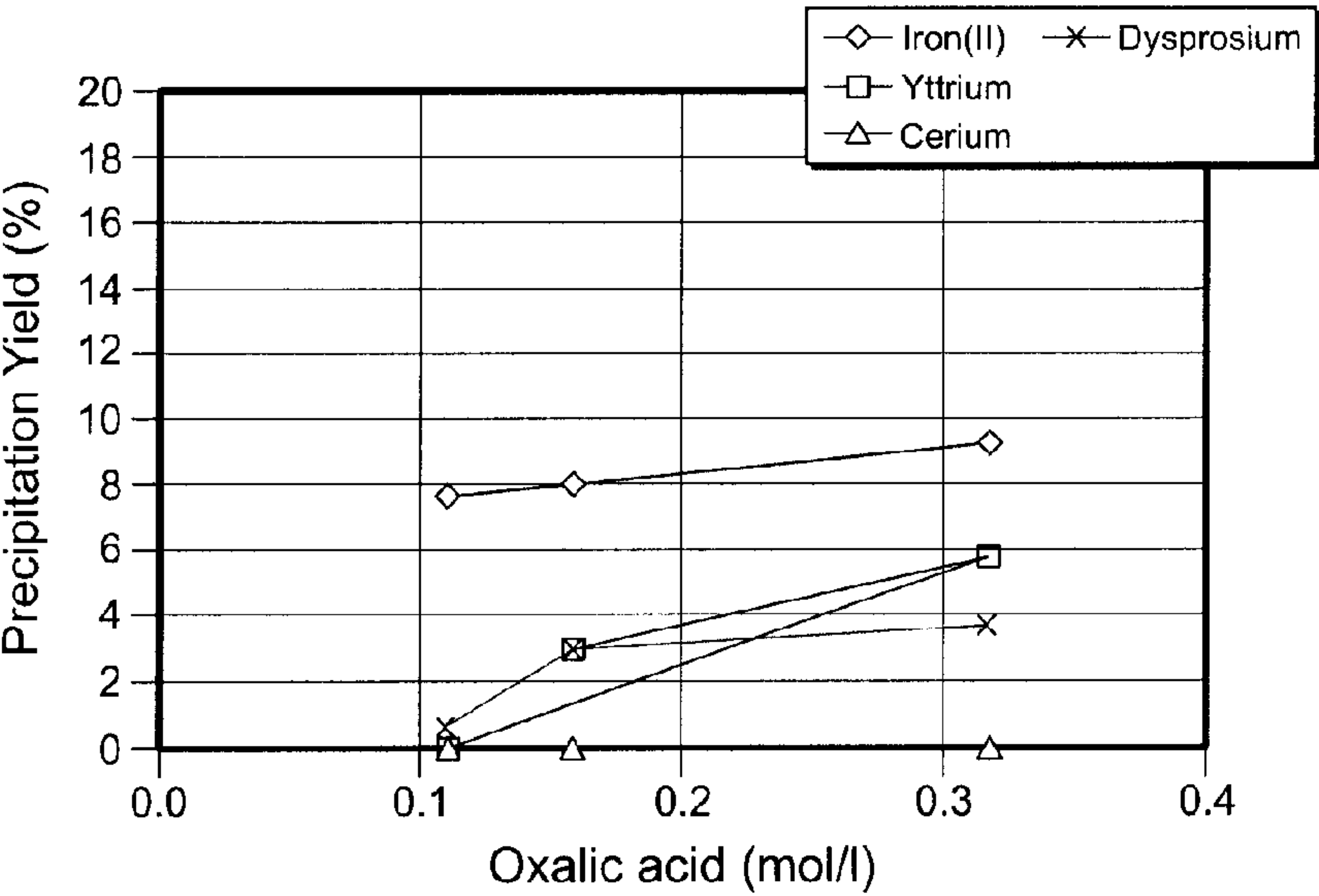
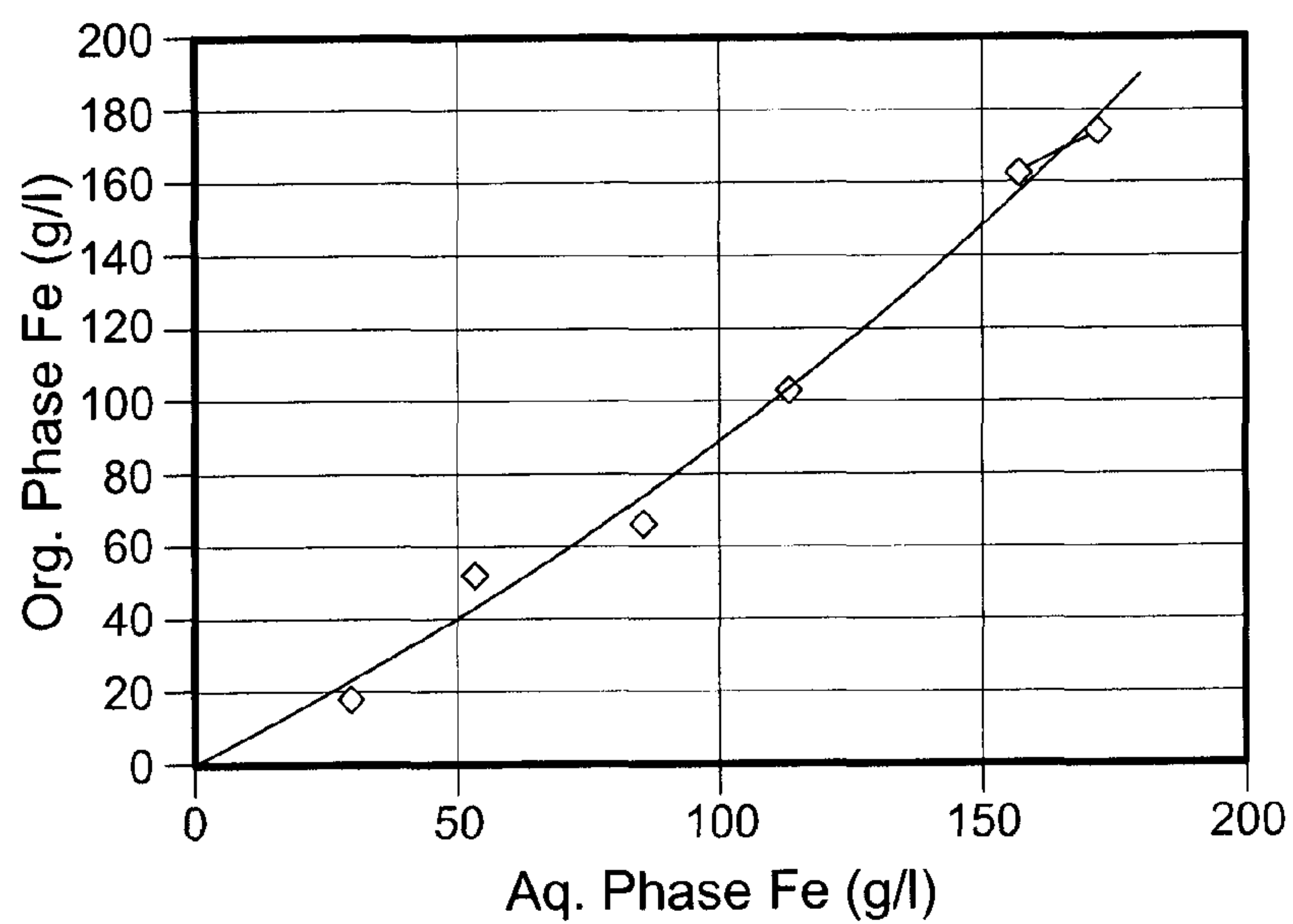
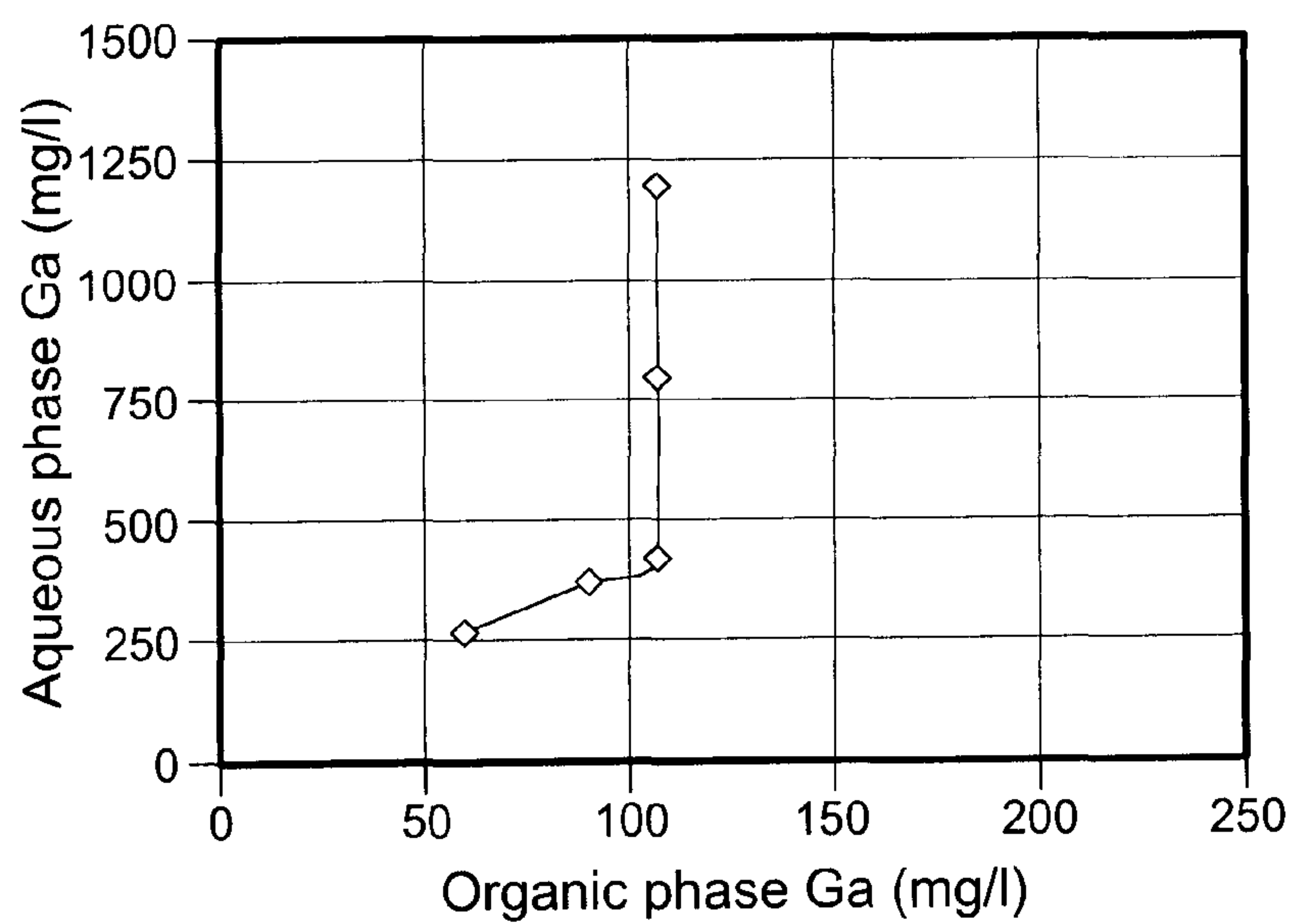


FIG. 11

**FIG. 12****FIG. 13**

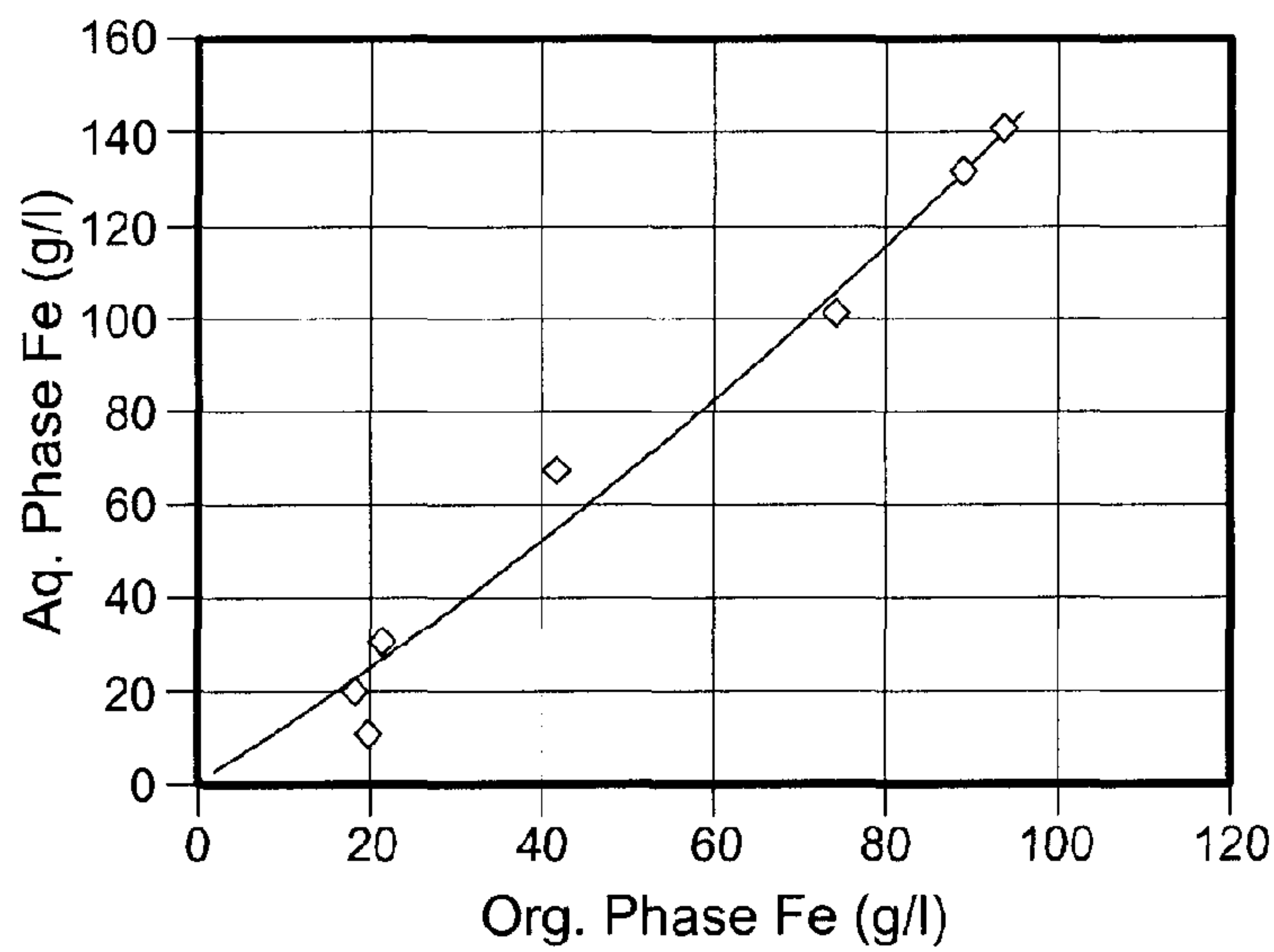


FIG. 14

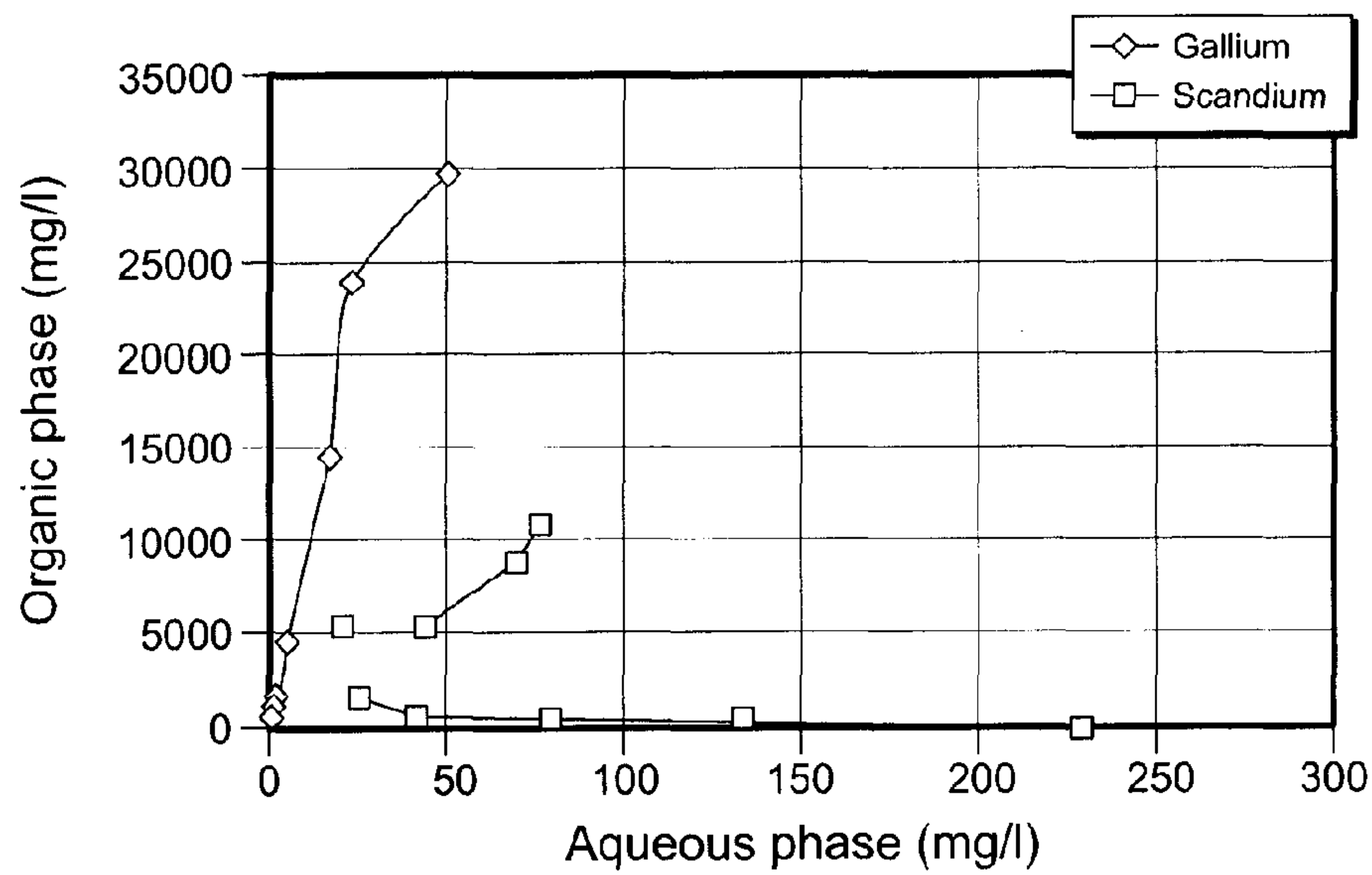
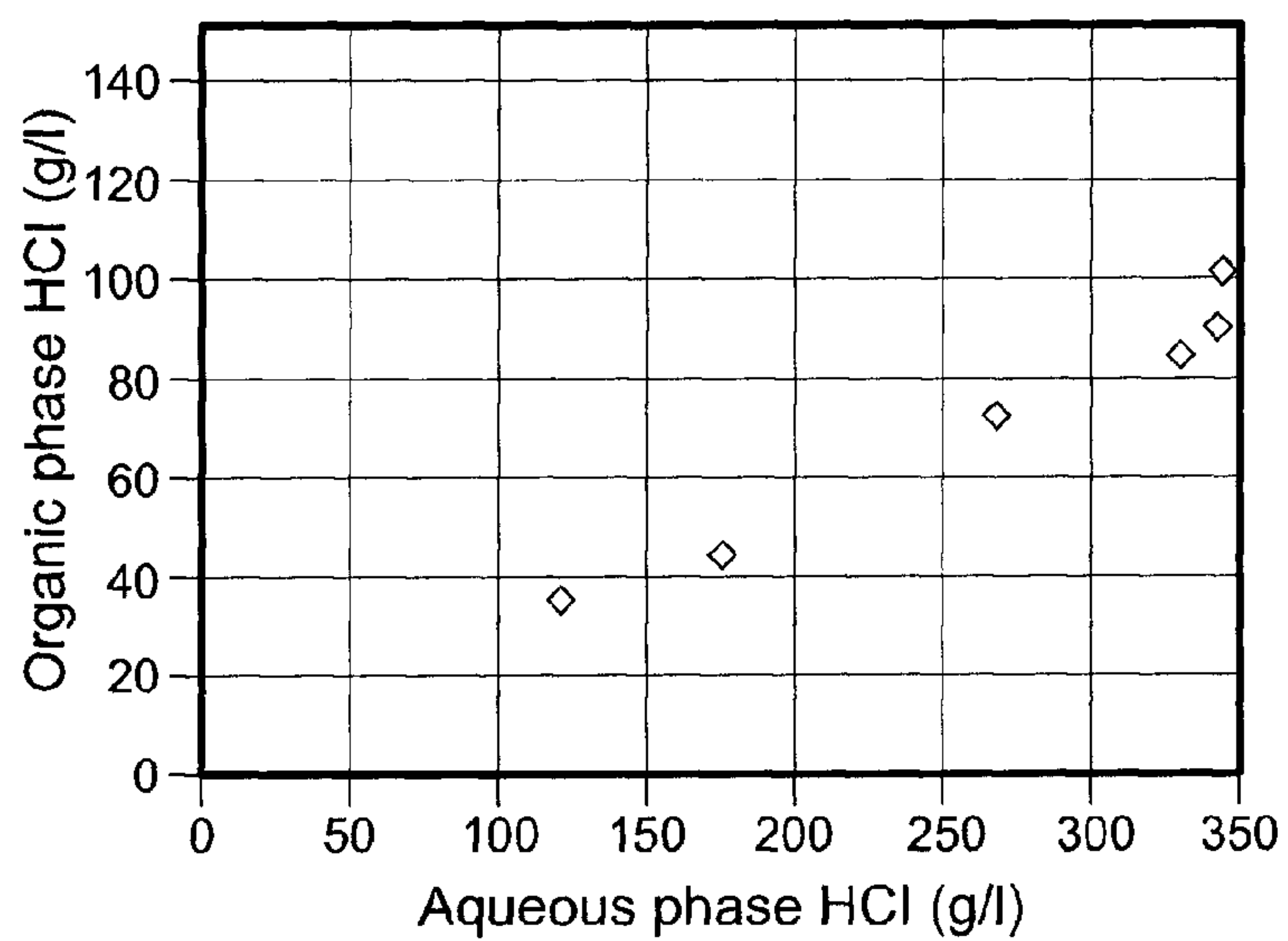
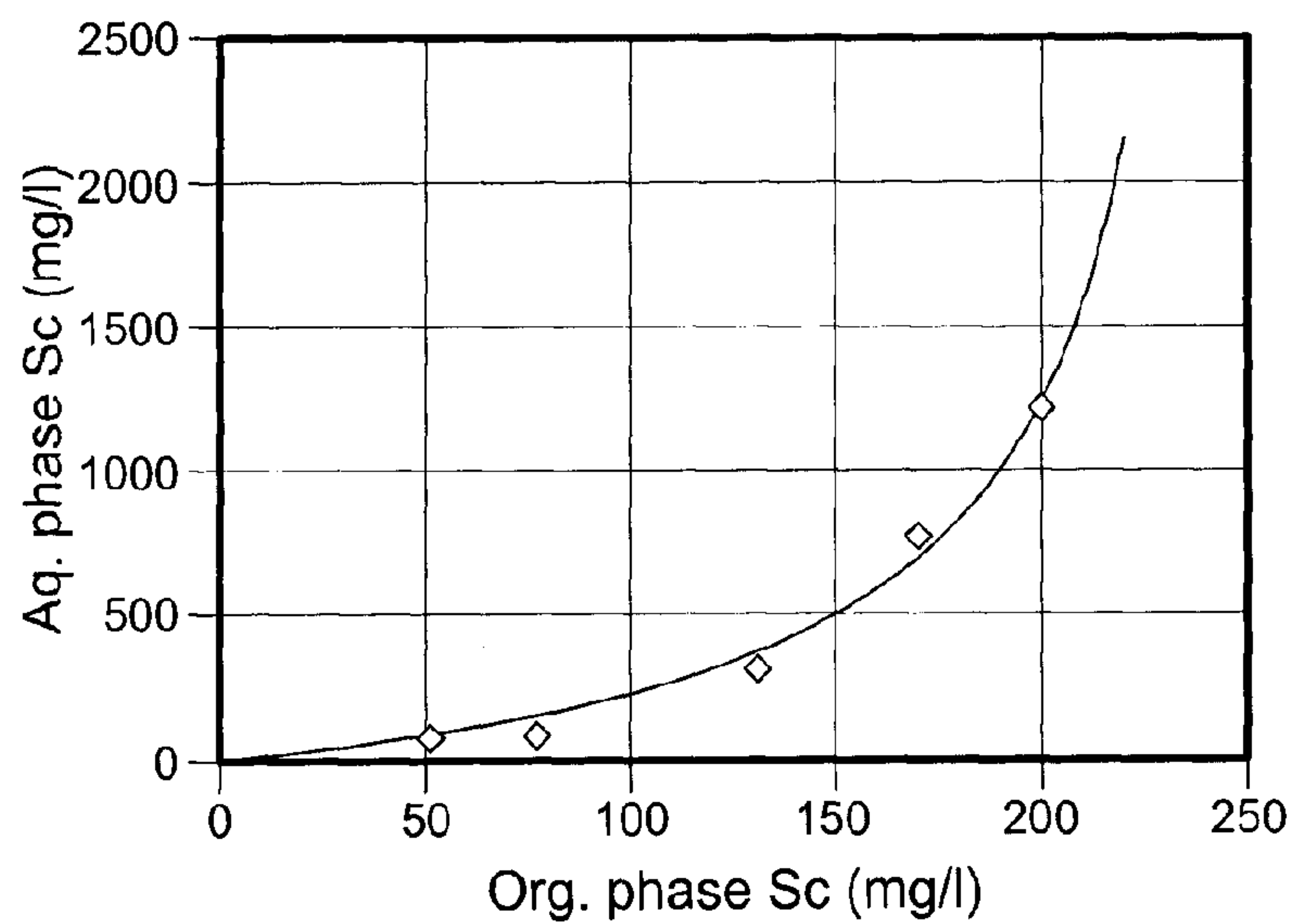


FIG. 15

**FIG. 16****FIG. 17**

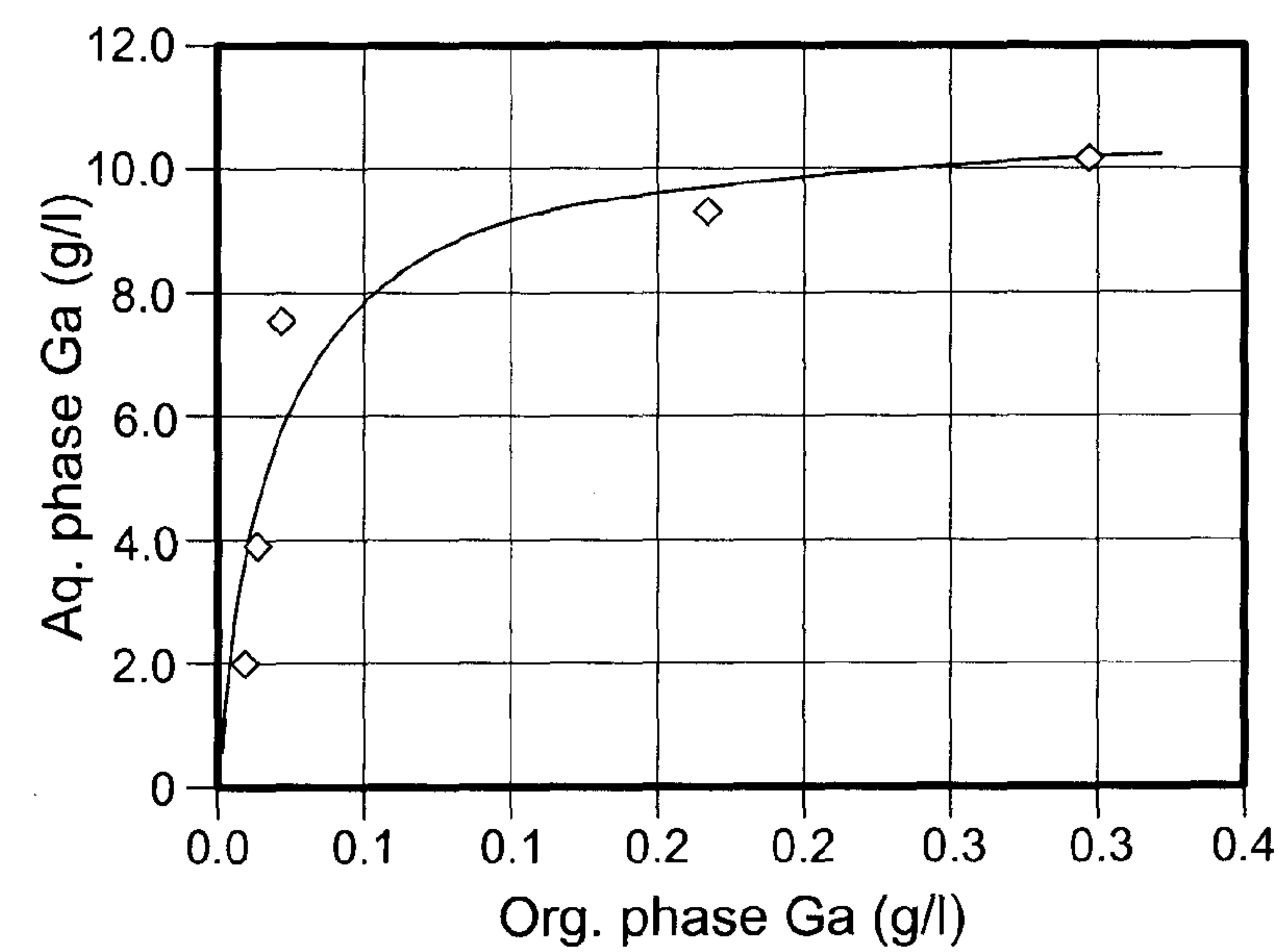


FIG. 18

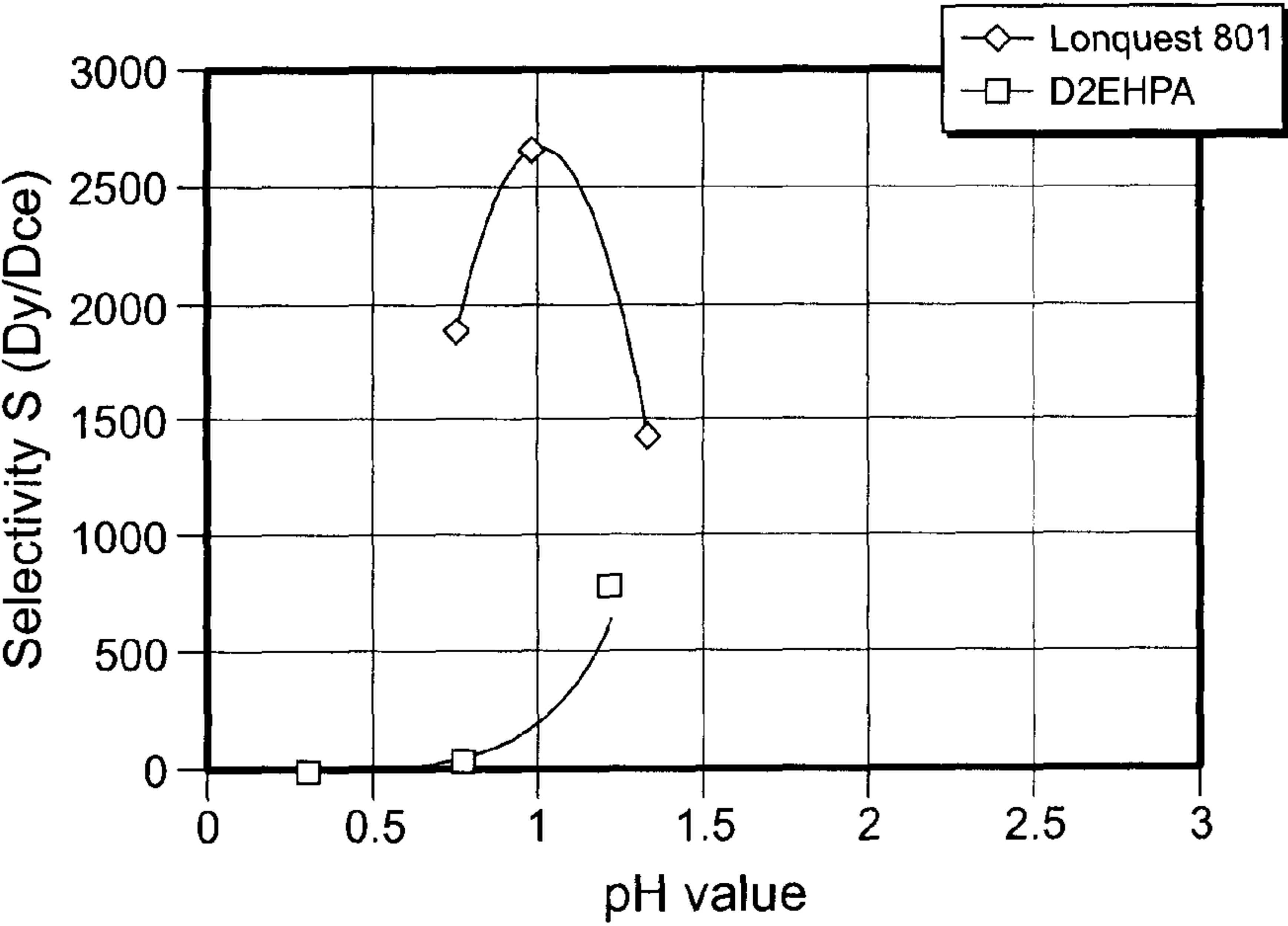


FIG. 19

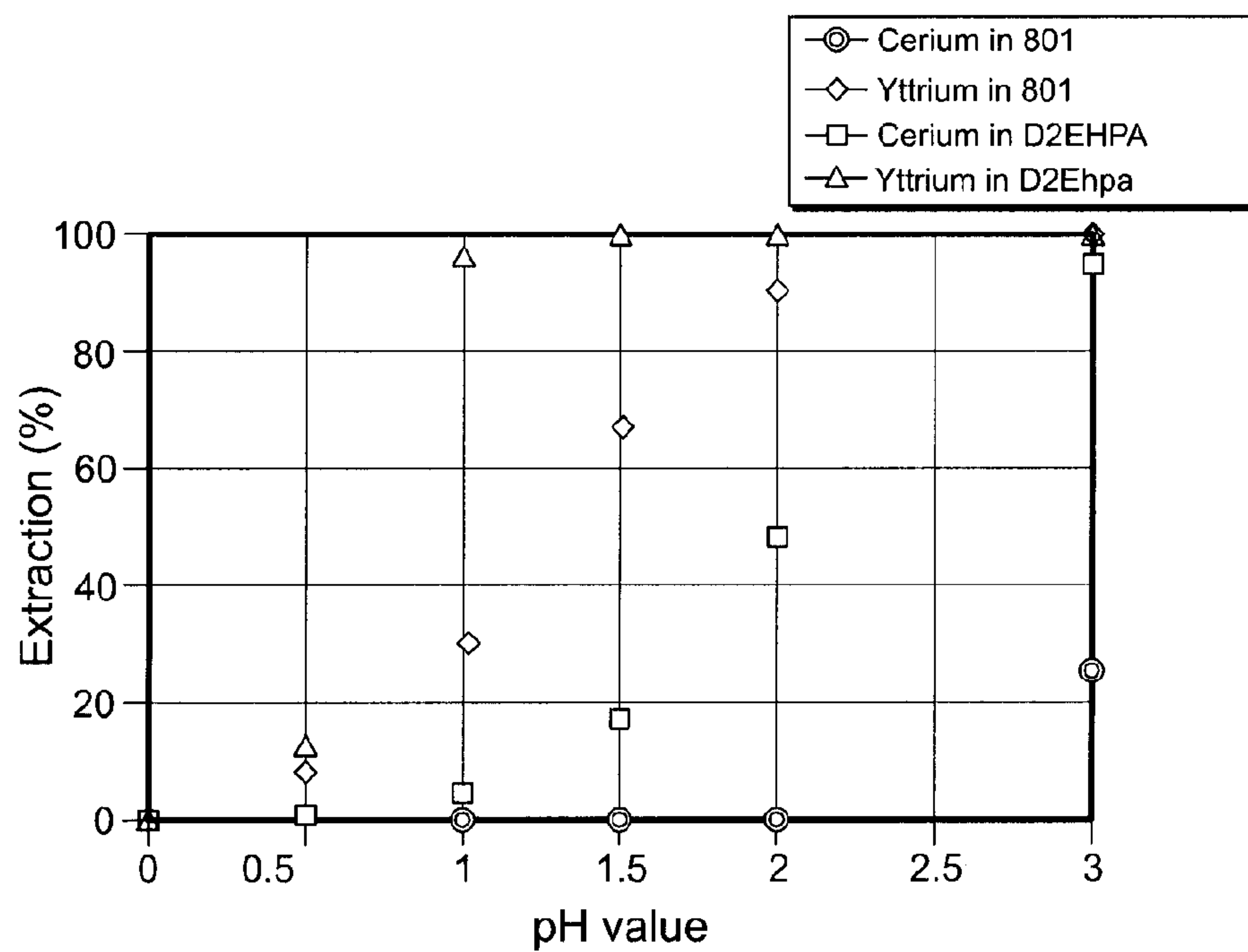


FIG. 20

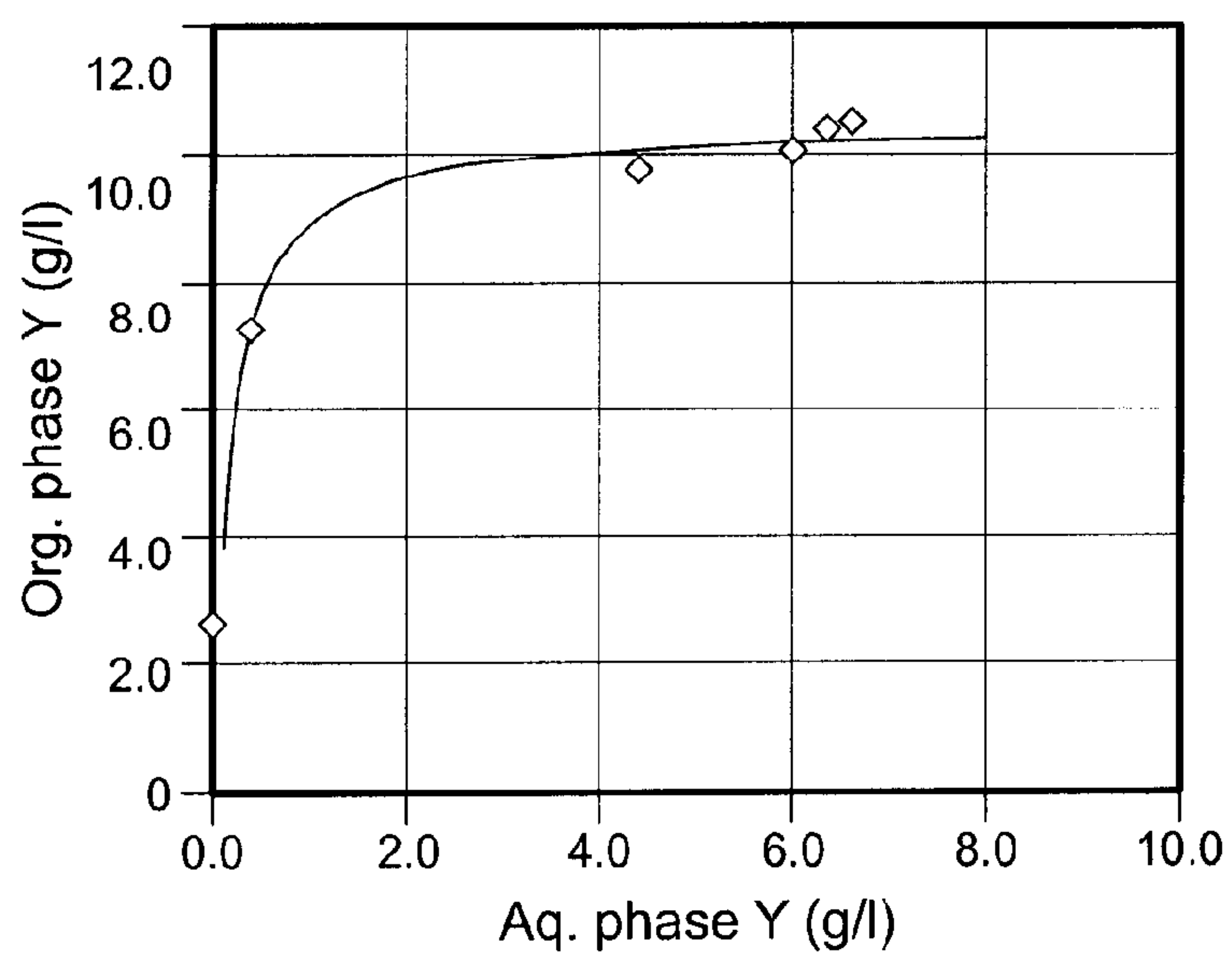


FIG. 21

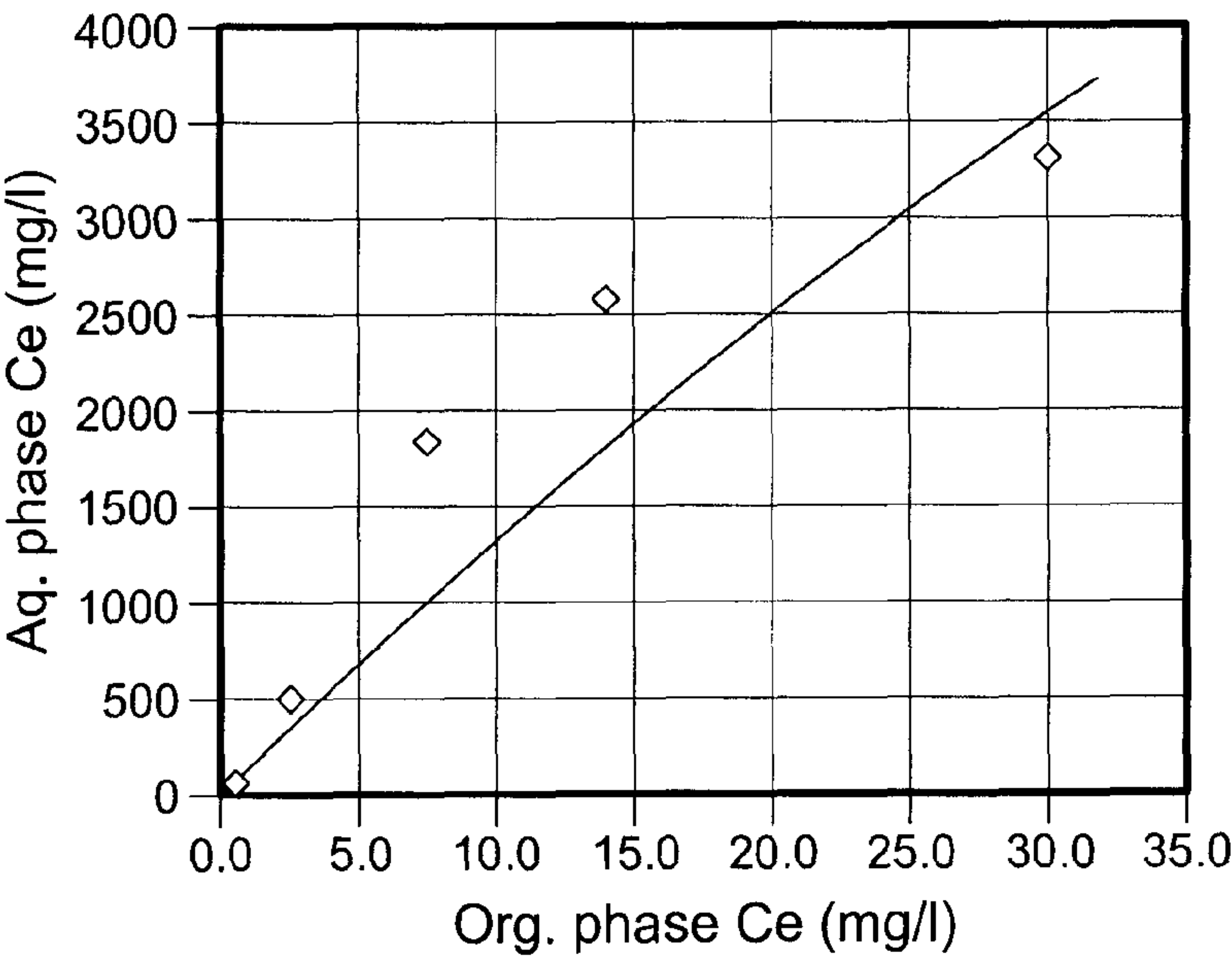


FIG. 22

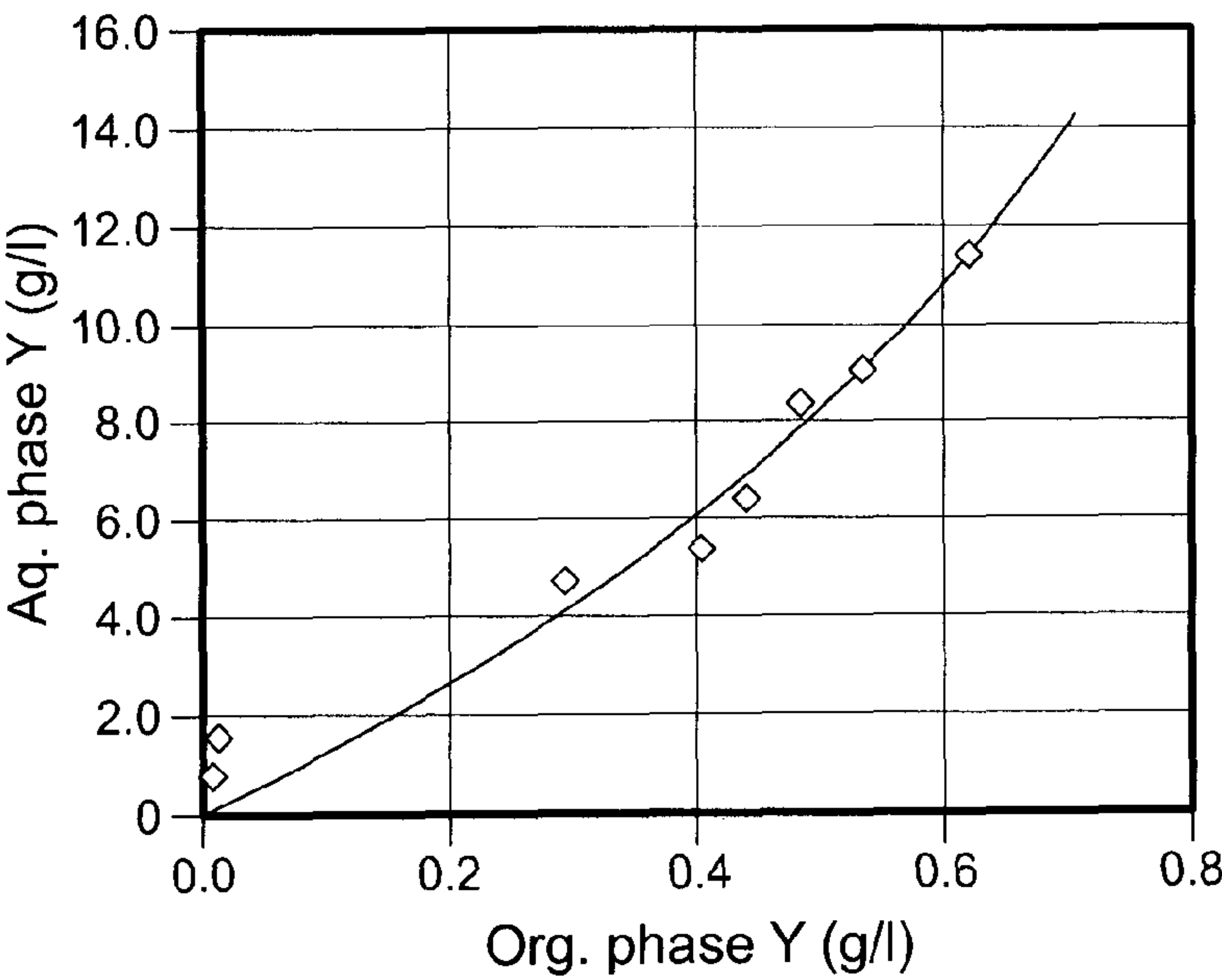


FIG. 23

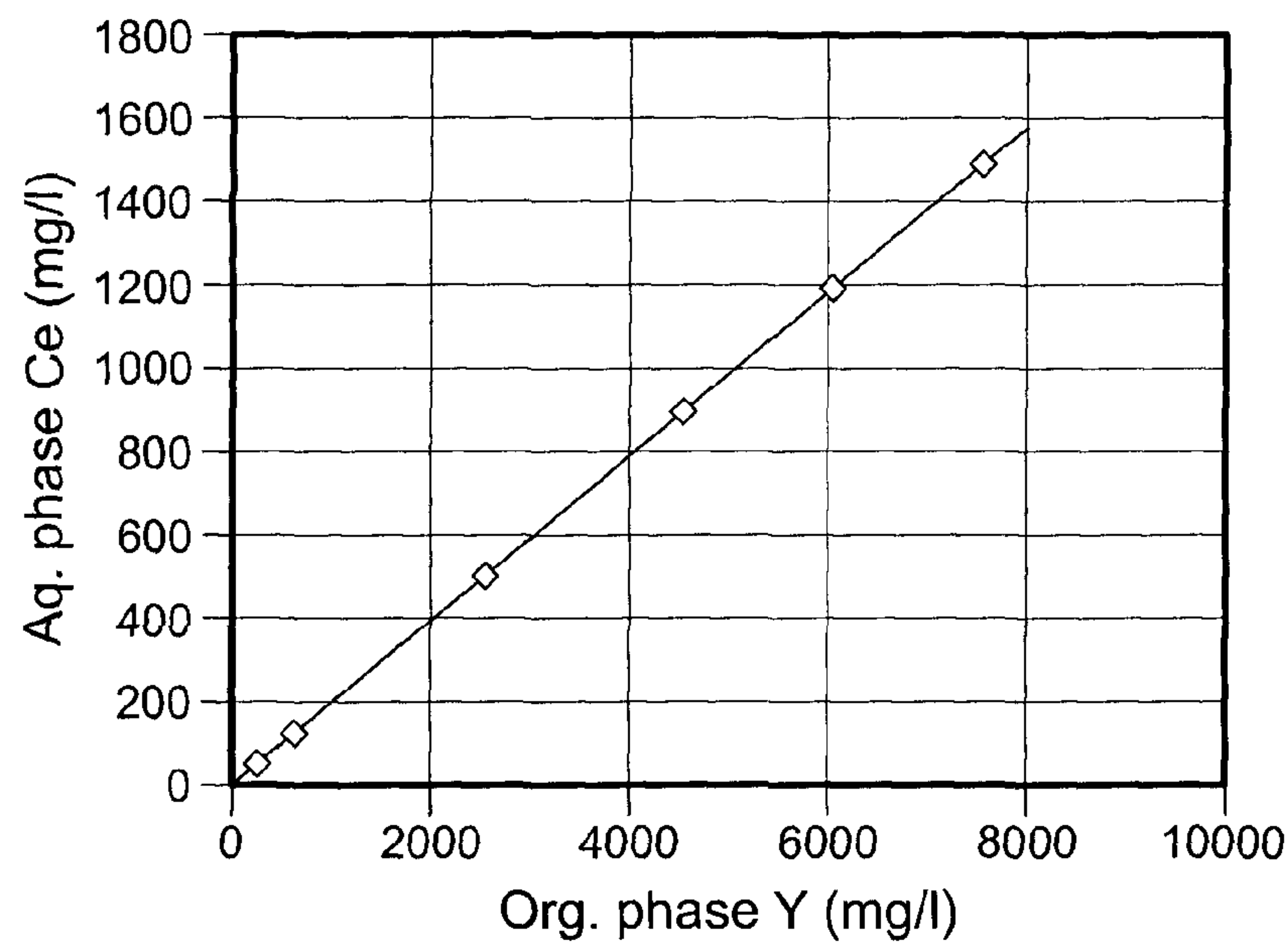


FIG. 24

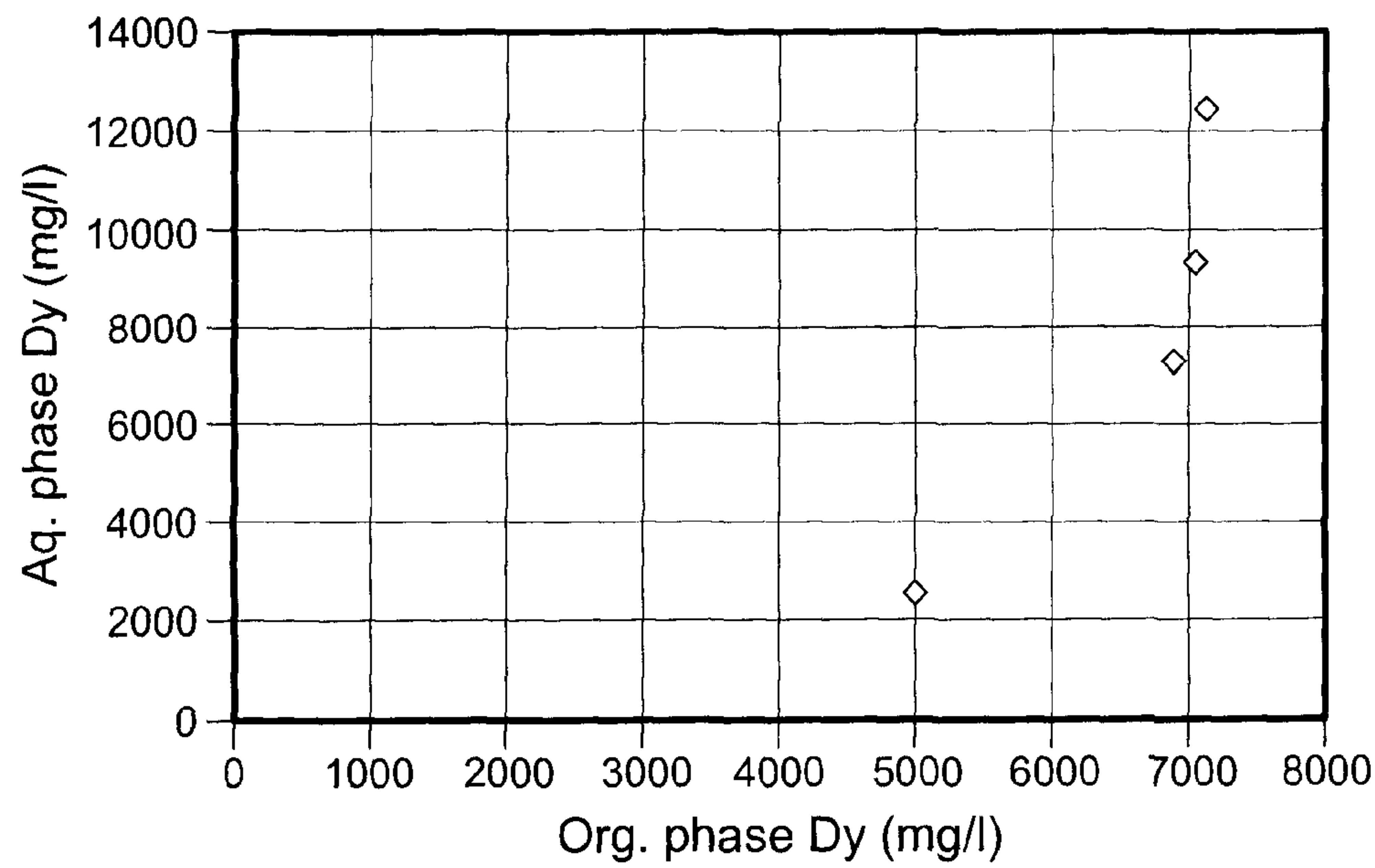


FIG. 25

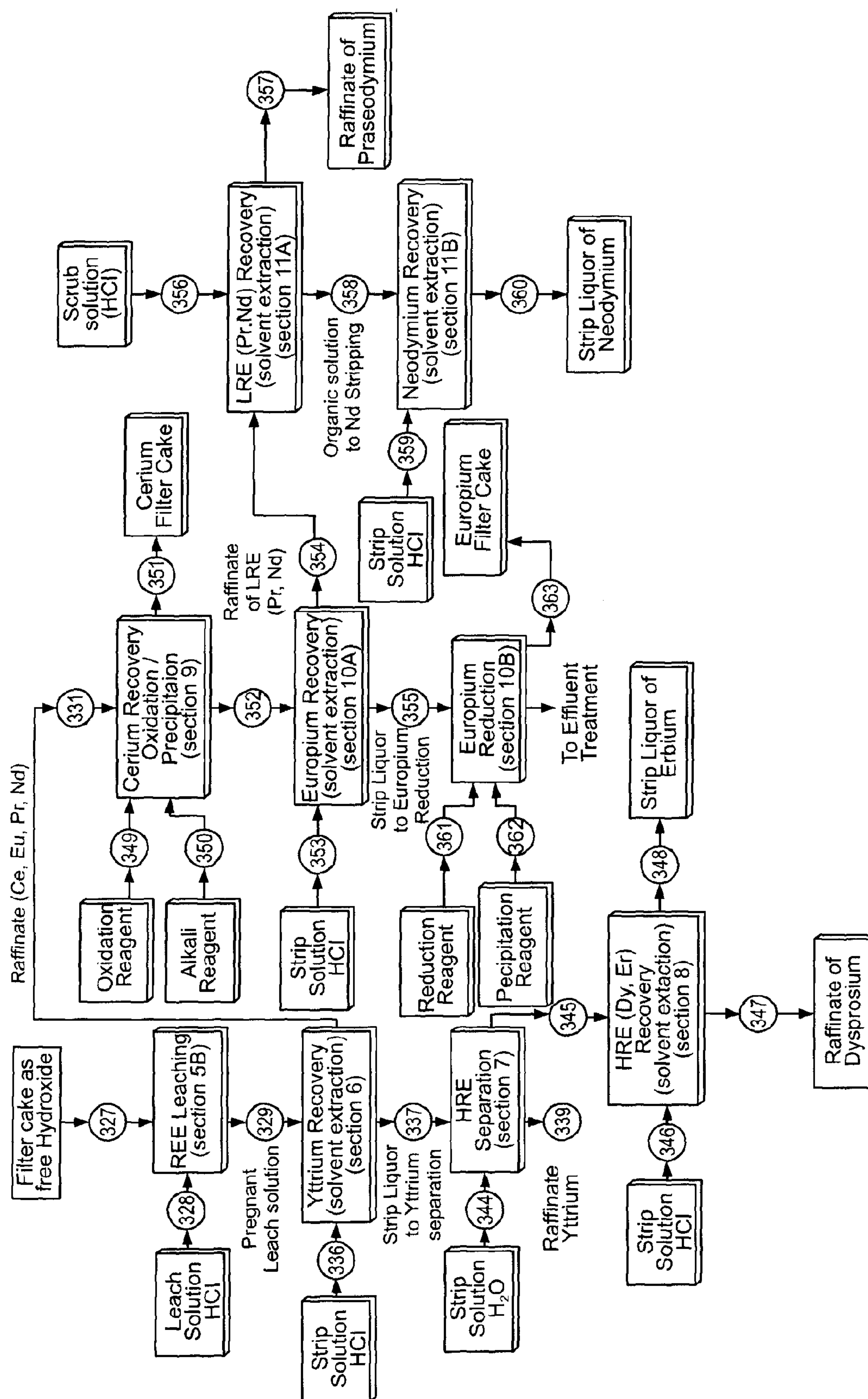


FIG. 26

PROCESSES FOR RECOVERING RARE EARTH ELEMENTS AND RARE METALS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] The present application claims priority on PCT/CA2012/000253 filed Mar. 19, 2012, on PCT/CA2012/000419 filed on May 3, 2012; on U.S. 61/703,219 filed on Sep. 19, 2012; and on U.S. 61/705,807 filed on Sep. 26, 2012. These documents are hereby incorporated by reference in their entirety.

TECHNICAL FIELD

[0002] The present disclosure relates to improvements in the field of chemistry applied to the recovery, extraction and/or isolation of rare earth elements (REE) and rare metals (RM). For example, such processes are useful for obtaining rare earth elements from various materials and derivatives thereof such as aluminum-containing materials and derivatives, iron-containing materials and derivatives, zinc-containing materials and derivatives thereof, copper-containing materials and derivatives thereof, nickel-containing materials and derivatives thereof, and titanium-containing materials and derivatives thereof.

BACKGROUND OF THE DISCLOSURE

[0003] In various technologies, there is an increasing need for rare earth elements. In few countries, efforts to reestablish mining of rare earth elements have been undertaken. In the future, supplies of rare earth elements will considerably depend upon economic viability of the extraction and production processes and technological innovations requiring such rare earth elements.

[0004] There is thus a need for providing an alternative to the existing solutions for extracting rare earth elements.

SUMMARY OF THE DISCLOSURE

[0005] According to one aspect, there is provided a process for recovering at least one rare earth element, the process comprising:

[0006] obtaining an acidic composition comprising (i) at least one rare earth element and optionally at least one rare metal; and

reacting the composition with a precipitating agent so as to substantially selectively precipitate a first rare earth element and optionally a first rare metal.

[0007] According to another aspect, there is provided a process for recovering at least one rare earth element, the process comprising:

[0008] obtaining an acidic composition comprising (i) at least one rare earth element and optionally at least one rare metal and (ii) at least one metal ion;

[0009] at least partially removing, from the acidic composition, the least one metal ion by means of an extracting agent, an ion exchange resin and/or by reacting the composition with a reducing agent, thereby obtaining a composition having a reduced content in the at least one metal ion; and

[0010] reacting the composition having the reduced content in the at least one metal ion with a precipitating agent so as to substantially selectively precipitate a first rare earth element and optionally a first rare metal.

[0011] According to another aspect, there is provided a process for recovering at least one rare earth element, the process comprising:

[0012] obtaining an acidic composition comprising (i) at least one rare earth element and optionally at least one rare metal and (ii) at least one iron ion;

[0013] at least partially removing, from the acidic composition, the least one iron ion by means of an extracting agent, an ion exchange resin and/or by reacting the composition with a reducing agent, thereby obtaining a composition having a reduced content in the at least one iron ion; and

[0014] reacting the composition having the reduced content in the at least one iron ion with a precipitating agent so as to substantially selectively precipitate a first rare earth element and optionally a first rare metal.

[0015] According to another aspect, there is provided a process for recovering at least one rare earth element from at least one material, the process comprising:

[0016] leaching the at least one material with at least one acid so as to obtain a leachate comprising at least one metal ion, and the at least one rare earth element;

[0017] substantially selectively precipitating, extracting and/or isolating the at least one metal ion from the leachate and optionally obtaining a precipitate; and

[0018] substantially selectively precipitating, extracting and/or isolating the at least one rare earth element from the leachate and/or the precipitate.

[0019] According to another aspect, there is provided a process for extracting at least one rare earth element from at least one material, the process comprising:

[0020] leaching the at least one material with at least one acid so as to obtain a leachate comprising at least one metal ion, and the at least one rare earth element; and

[0021] selectively precipitating at least one member chosen from the at least one rare earth element, and the at least one metal ion.

[0022] According to one aspect, there is provided a process for recovering at least one rare earth element from at least one material, the process comprising:

[0023] leaching the at least one material with at least one acid so as to obtain a leachate comprising at least one metal ion, and at least one rare earth element;

[0024] optionally substantially selectively precipitating, extracting and/or isolating the at least one rare earth element from the leachate and/or the precipitate.

[0025] substantially selectively precipitating, extracting and/or isolating the at least one metal ion from the leachate and optionally obtaining a precipitate; and

[0026] substantially selectively precipitating, extracting and/or isolating the at least one rare earth element from the leachate and/or the precipitate.

[0027] According to another example, there is provided a process for recovering at least one rare earth element from at least one material, the process comprising:

[0028] leaching the at least one material with at least one acid so as to obtain a leachate comprising at least one metal ion, the at least one rare earth element, and a solid, and separating the leachate from the solid;

[0029] substantially selectively removing at least one metal ion from the leachate and optionally obtaining a precipitate; and

[0030] substantially selectively removing the at least one rare earth element from the leachate and/or the precipitate.

[0031] According to another example, there is provided process for recovering at least one rare earth element from at least one material, the process comprising:

[0032] leaching the at least one material with at least one acid so as to obtain a leachate comprising at least one metal ion and the at least one rare earth element, and a solid, and separating the leachate from the solid; and

[0033] substantially selectively removing at least one member chosen from the at least one rare earth element and the at least one metal ion from the leachate.

BRIEF DESCRIPTION OF DRAWINGS

[0034] In the following drawings, which represent by way of example only, various embodiments of the disclosure:

[0035] FIG. 1 shows a bloc diagram of an example of a process for preparing alumina and various other products including rare earth elements, according to the present disclosure;

[0036] FIG. 2 shows a bloc diagram of another example of process for preparing alumina and various other products including rare earth elements, according to the present disclosure;

[0037] FIGS. 2A and 2B show a bloc diagram of a process similar to the process shown in FIG. 2;

[0038] FIG. 3 shows a bloc diagram of another example of process for extracting rare earth elements according to the present disclosure;

[0039] FIG. 3A shows a bloc diagram of a process similar to the process shown in FIG. 3;

[0040] FIGS. 4A and 4B show a bloc diagram of another example of a process for extracting rare earth elements according to the present disclosure;

[0041] FIGS. 4C and 4D show a bloc diagram of processes similar to those shown in FIGS. 4A and 4B;

[0042] FIGS. 5A, 5B, 5C, 5D show a bloc diagram of another example of a process for extracting rare earth elements according to the present disclosure;

[0043] FIGS. 5E, 5F, 5G and 5H show a bloc diagram of processes similar to those shown in FIGS. 5A, 5B, 5C, and 5D;

[0044] FIGS. 6 to 11 represents precipitation yields (%) obtained for various rare earth elements and rare metals, during processes according to the present disclosure;

[0045] FIGS. 12 to 25 represent curves showing various results obtained when carrying out extractions of compounds, during processes according to the present disclosure; and

[0046] FIG. 26 shows a bloc diagram of another example of process for extracting rare earth elements according to the present disclosure.

DETAILED DESCRIPTION OF VARIOUS EMBODIMENTS

[0047] Further features and advantages will become more readily apparent from the following description of various embodiments as illustrated by way of examples.

[0048] It was found that that the rare earth element(s) recovery can be made, for example, in the processes described in the present disclosure at various stages. Moreover, it was found that such processes can be useful even if the rare earth elements are only found as traces. It was also found that such processes can be particularly useful for extracting rare earth elements from a solution that is substantially refined or purified. For example, these processes can be useful

since they can be applied to solutions from which several of the main components have been removed. They can also be applied to solutions before removal of several of the main components.

[0049] The expression “at least one metal ion”, as used herein refers, for example, to at least one type of ion chosen from all possible forms of ions of such a metal. For example, if the metal “M” can be M^{2+} or M^{3+} , the at least one metal ion for the metal M can be either M^{2+} or M^{3+} . For example, the metal can be chosen from aluminum, iron, zinc, copper, nickel, magnesium, titanium etc.

[0050] The expression “at least one aluminum ion”, as used herein refers, for example, to at least one type of aluminum ion chosen from all possible forms of Al ions. For example, the at least one aluminum ion can be Al^{3+} .

[0051] The expression “at least one iron ion”, as used herein refers, for example, to at least one type of iron ion chosen from all possible forms of Fe ions. For example, the at least one iron ion can be Fe^{2+} , Fe^{3+} , or a mixture thereof.

[0052] The expression “at least one zinc ion”, as used herein refers, for example, to at least one type of zinc ion chosen from all possible forms of Zn ions. For example, the at least one zinc ion can be Zn^{2+} .

[0053] The expression “at least one copper ion”, as used herein refers, for example, to at least one type of copper ion chosen from all possible forms of Cu ions. For example, the at least one copper ion can be Cu^{1+} or Cu^{2+} , or a mixture thereof.

[0054] The expression “at least one nickel ion”, as used herein refers, for example, to at least one type of nickel ion chosen from all possible forms of Ni ions. For example, the at least one nickel ion can be Ni^{2+} or Ni^{3+} , or a mixture thereof.

[0055] The expression “at least one magnesium ion”, as used herein refers, for example, to at least one type of magnesium ion chosen from all possible forms of Mg ions. For example, the at least one magnesium ion can be Mg^{2+} .

[0056] The expression “at least one titanium ion”, as used herein refers, for example, to at least one type of titanium ion chosen from all possible forms of Ti ions. For example, the at least one titanium ion can be Ti^{3+} or Ti^{4+} , or a mixture thereof.

[0057] The expression “at least one rare earth element”, as used herein refers, for example, to at least one type of rare earth element chosen from all the rare earth elements described in the present disclosure in all their possible forms.

[0058] The expression “at least one rare metal”, as used herein refers, for example, to at least one type of rare metal chosen from all the rare metals described in the present disclosure in all their possible forms.

[0059] The expression “Ga-free solution”, as used herein refers, for example, to a solution that comprises about less than 5%, 2% or 1% w/v of gallium.

[0060] The expression “Ce-free solution”, as used herein refers, for example, to a solution that comprises about less than 5%, 2% or 1% w/v of cerium.

[0061] The expression “Sc-free solution”, as used herein refers, for example, to a solution that comprises about less than 5%, 2% or 1% w/v of scandium.

[0062] The expression “Sm-free solution”, as used herein refers, for example, to a solution that comprises about less than 5%, 2% or 1% w/v of samarium.

[0063] The expression “Eu-free solution”, as used herein refers, for example, to a solution that comprises about less than 5%, 2% or 1% w/v of europium.

[0064] The expression “Gd-free solution”, as used herein refers, for example, to a solution that comprises about less than 5%, 2% or 1% w/v of gadolinium.

[0065] The expression “Y-free solution”, as used herein refers, for example, to a solution that comprises about less than 5%, 2% or 1% w/v of yttrium.

[0066] The expression “Pr-free solution”, as used herein refers, for example, to a solution that comprises about less than 5%, 2% or 1% w/v of praseodymium.

[0067] The expression “Nd-free solution”, as used herein refers, for example, to a solution that comprises about less than 5%, 2% or 1% w/v of neodymium.

[0068] The expression “La-free solution”, as used herein refers, for example, to a solution that comprises about less than 5%, 2% or 1% w/v of lanthanum.

[0069] The expression “Er-free solution”, as used herein refers, for example, to a solution that comprises about less than 5%, 2% or 1% w/v of erbium.

[0070] The expression “Dy-free solution”, as used herein refers, for example, to a solution that comprises about less than 5%, 2% or 1% w/v of dysprosium.

[0071] The expression “rare earth element” as used herein refers, for example, to a rare element chosen from scandium, yttrium, lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium. The acronym “REE” can be used in the present disclosure as a synonym for “rare earth element”.

[0072] The expression “rare metal” as used herein refers, for example, to a rare metal chosen from indium, zirconium, lithium, and gallium. These rare metals can be in various form such as the elemental form (or metallic form), under the form of halides (for example chlorides), oxides, sulfates, oxalates, hydroxides etc. The acronym “RM” can be used in the present disclosure as a synonym for “rare metal”.

[0073] The term “REEO or REE-O” as used in the present disclosure refers to rare earth element oxide(s).

[0074] The term “RMO or RM-O” as used in the present disclosure refers to rare metal oxide(s).

[0075] Terms of degree such as “about” and “approximately” as used herein mean a reasonable amount of deviation of the modified term such that the end result is not significantly changed. These terms of degree should be construed as including a deviation of at least $\pm 5\%$ or at least $\pm 10\%$ of the modified term if this deviation would not negate the meaning of the word it modifies.

[0076] In the processes of the present disclosure, after the leaching, the substantially selectively removing of the at least one member chosen from the at least one rare earth element and the at least one metal from the leachate can be made in various manners. The at least one metal ion (or a second metal ion) can be removed and then, a first metal ion can be removed and finally, the at least one rare earth element can be removed. Alternatively, the first metal ion can be removed, then the second metal ion can be removed and finally, the at least one rare earth element can be removed. According to another example, the at least one rare earth element can be removed, then, the first metal ion can be removed, and finally the second metal ion can be removed. Also, the at least one rare earth element can be removed, then, the second metal ion can be removed, and finally the first metal ion can be removed. Various other possible combinations can also be envisaged.

[0077] The at least one acid used for leaching the at least one material can be HCl, H₂SO₄, HNO₃ or mixtures thereof.

More than one acid can be used as a mixture or separately. Solutions made with these acids can be used at various concentration. For example, concentrated solutions can be used. For example, 6 M or 12 M HCl can be used. For example, up to 98% or 100% wt H₂SO₄ can be used. For example, 18 wt % or 32 wt % can be used.

[0078] For example, the at least one material can be leached with HCl having a concentration of about 15 to about 45 weight %, of about 20 to about 45 weight %, of about 25 to about 45 weight %, of about 26 to about 42 weight %, of about 28 to about 40 weight %, of about 30 to about 38 weight %, or between 25 and 36 weight %.

[0079] Leaching can also be carried out by adding dry highly concentrated acid (for example, 85%, 90% or 95%) in gas phase into the aqueous solution. Alternatively, leaching can also be carried out by using a weak acid solution (for example <3 wt %).

[0080] For example, leaching can be carried out by using HCl having a concentration of about 18 to about 32 wt % in a first reactor and then, by using HCl having concentration of about 90 to about 95% in a second reactor.

[0081] For example, the at least one material can be leached at a temperature of about 125 to about 225° C., about 150 to about 200° C., about 160 to about 180° C., or about 165 to about 170° C.

[0082] For example, the leaching can be carried out under pressure. For example, the pressure can be about 100 to about 300 or about 150 to about 200 psig. The leaching can be carried out for about 30 minutes to about 5 hours. For example, the leaching can be carried out at a temperature of about 60° C. to about 200° C.

[0083] For example, the leaching can be carried out under pressure into an autoclave. For example, it can be carried out at a pressure of 5 KPag to about 850 KPag, 50 KPag to about 800 KPag, 100 KPag to about 750 KPag, 150 KPag to about 700 KPag, 200 KPag to about 600 KPag, or 250 KPag to about 500 KPag.

[0084] For example, the leaching can be carried out at a temperature of at least 80° C., at least 90° C., or about 100° C. to about 110° C. In certain cases it can be done at higher temperatures so as to increase extraction yields of rare earth elements in certain ores. For example, the leaching can be carried out at a temperature of at least 100° C., at least 120° C., at least 130° C., at least 140° C., or about 140° C. to about 175° C.

[0085] For example, in the leachate, the at least one rare earth element can be in the form of an ion.

[0086] For example, after the leaching, the at least one rare earth element can be solubilized into the solution and can be found as a soluble ion, associated to chlorine, a sulfate, a nitrate, or hydrates thereof. etc.

[0087] For example, after the leaching, (if required) various bases can be used for raising up the pH such as KOH, NaOH, Ca(OH)₂, CaO, MgO, Mg(OH)₂, CaCO₃, Na₂CO₃, NaHCO₃, CO₂, or mixtures thereof.

[0088] For example, the at least one material can be chosen from aluminum-containing materials and derivatives, iron-containing materials and derivatives, zinc-containing materials and derivatives thereof, copper-containing materials and derivatives thereof, nickel-containing materials and derivatives thereof, magnesium-containing materials and derivatives thereof and titanium-containing materials and derivatives thereof.

[0089] For example, the at least one aluminum-containing material can be at least one aluminum-containing ore.

[0090] For example, the at least one iron-containing material can be at least one iron-containing ore.

[0091] For example, the at least one zinc-containing material can be at least one zinc-containing ore.

[0092] For example, the at least one copper-containing material can be at least one copper-containing ore.

[0093] For example, the at least one nickel-containing material can be at least one nickel-containing ore.

[0094] For example, the at least one magnesium-containing material can be at least one magnesium-containing ore.

[0095] For example, the at least one titanium-containing material can be at least one titanium-containing ore.

[0096] For example, the at least one metal ion can comprise at least one aluminum ion, at least one zinc ion, at least one copper ion, at least one nickel ion, at least one magnesium ion, at least one titanium ion and/or at least one iron ion.

[0097] For example, the at least one metal ion can comprise a first metal ion and a second metal ion.

[0098] For example, the first metal ion can comprise at least one aluminum ion, at least one zinc ion, at least one copper ion, at least one nickel ion, at least one titanium ion and/or at least one iron ion.

[0099] For example, the second metal ion can comprise at least one aluminum ion, at least one zinc ion, at least one copper ion, at least one nickel ion, at least one titanium ion and/or at least one iron ion.

[0100] For example, the first metal ion can be at least one aluminum ion.

[0101] For example, the second metal ion can be at least one iron ion.

[0102] For example, the at least one metal ion can be removed by using an ion exchange resin or ion exchange system. For example, such an ion exchange resin or system can be effective for allowing only chlorides of rare earth elements and chlorides rare metals to pass therethrough, while capturing the at least one metal ion.

[0103] For example, the at least one iron ion can be precipitated. When precipitating the at least one iron ion, it can be precipitated by means of an ionic precipitation and it can precipitate in the form of various salts, hydroxides, chlorides or hydrates thereof. For example, the at least one iron ion can be precipitated as FeCl_2 , FeCl_3 , $\text{Fe}(\text{OH})_3$, $\text{Fe}(\text{OH})_2$, hematite, goetite, jarosite or hydrates thereof.

[0104] For example, after the precipitation of the at least one iron ion, the at least one rare earth element can be solubilized into the solution and can be found as a soluble ion, associated as an hydroxide or a salt, or hydrates thereof.

[0105] For example, the at least aluminum ion can be precipitated. When precipitating the at least aluminum ion, it can be precipitated by means of an ionic precipitation and it can precipitate in the form of various salts, (such as chlorides, sulfates) or hydroxides or hydrates thereof. For example, the at least one aluminum ion can be precipitated as $\text{Al}(\text{OH})_3$, $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{Al}_2(\text{SO}_4)_3$, or hydrates thereof.

[0106] For example, after the precipitation of the at least one metal ion, the at least one rare earth element can be solubilized into the solution and can be found as a an ion associated to an hydroxide or a salt or hydrates thereof.

[0107] For example, after precipitation of the at least one metal ion, the residual and substantially purified or refined solution can contain the at least one rare earth element into a mixture of residual soluble ions, such as Cl^- , SO_4^{2-} , Na^+ .

[0108] The processes of the present disclosure can be effective for treating various materials. The at least one material can be an aluminum-containing material, The aluminum-containing material can be an aluminum-containing ore. For example, clays, argillite, mudstone, beryl, cryolite, garnet, spinel, bauxite, or mixtures thereof can be used as starting material. The aluminum-containing material can also be a recycled industrial aluminum-containing material such as slag. The aluminum-containing material can also be red mud.

[0109] The processes of the present disclosure can be effective for treating various nickel-containing ores. For example, niccolite, kamacite, taenite, limonite, garnierite, laterite, pentlandite, or mixtures thereof can be used.

[0110] The processes of the present disclosure can be effective for treating various zinc-containing ores. For example, smithsonite, warikahnite, sphalerite, or mixtures thereof can be used.

[0111] The processes of the present disclosure can be effective for treating various copper-containing ores. For example, copper-containing oxide ores, can be used. For example, chalcopyrite, chalcocite, covellite, bornite, tetrahedrite, malachite, azurite, cuprite, chrysocolla, or mixtures thereof can also be used.

[0112] The processes of the present disclosure can be effective for treating various magnesium-containing materials. For example, the serpentine can be treated by such processes. Moreover, antigorite, chrysotile and lizardite can also be treated by such processes as well as various magnesium waste materials and reject such as industrial or mining wastes and mixtures thereof.

[0113] The processes of the present disclosure can be effective for treating various titanium-containing ores. For example, ecandrewsite, geikielite, pyrophanite, ilmenite, rutile or mixtures thereof can be used.

[0114] For example, the at least one rare earth element can be chosen from scandium, yttrium, lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium.

[0115] For example, the at least one rare metal can be chosen from indium, zirconium, lithium, and gallium.

[0116] For example, rare earth elements can sometimes be divided into two categories, light rare earth elements (LRE) and heavy rare earth elements (HRE). The light rare earth elements can comprise lanthanum, cerium, praseodymium, neodymium, and samarium (atomic numbers 57-62), and they are usually more abundant than heavy ones.

[0117] For example, the at least one rare element can be extracted under the form of various salts, oxides, hydroxides, and hydrates thereof.

[0118] For example, the at least one rare earth element can be chosen from scandium, gallium, yttrium, lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, dysprosium, erbium, ytterbium and mixtures thereof.

[0119] For example, the at least one rare earth element is chosen from scandium, gallium, yttrium, lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, dysprosium and mixtures thereof.

[0120] For example, the at least one rare earth element is chosen from scandium, gallium, yttrium, cerium and mixtures thereof.

[0121] For example, the at least one rare earth element can be yttrium.

[0122] For example, the at least one rare earth element can be scandium.

[0123] For example, the at least one rare earth element can be gallium.

[0124] For example, the at least one rare earth element can be cerium.

[0125] For example, the processes can comprise:

[0126] leaching the at least one material with HCl so as to obtain the leachate comprising the at least one metal ion, and the at least one rare earth element, and the solid and separating the leachate from the solid;

[0127] substantially selectively removing the at least one metal ion from the leachate, thereby obtaining a composition comprising the metal ion, and the at least one rare earth element; and

[0128] substantially selectively at least partially removing the at least one metal ion from the composition, thereby obtaining a liquor comprising the at least one rare earth element.

[0129] For example, the at least one metal ion can be substantially selectively removed from the leachate by substantially selectively precipitating it from the leachate and removing it therefrom by carrying out a solid-liquid separation.

[0130] For example, the at least one metal ion can be substantially selectively removed from the leachate by substantially selectively precipitating it under the form of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ and removing it therefrom by carrying out a solid-liquid separation.

[0131] For example, the composition can comprise HCl, the at least one metal ion, and the at least one rare earth element.

[0132] For example, the composition can be an acidic composition that comprises, the at least one metal ion, and the at least one rare earth element.

[0133] For example, the acidic composition can comprises (i) the at least one rare earth element and optionally that least one rare metal and (ii) FeCl_3 .

[0134] For example, the at least one iron ion can be substantially selectively removed from the composition by carrying out an hydrolysis so as to convert the at least one iron ion into Fe_2O_3 and removing the precipitated Fe_2O_3 from the composition by carrying out a solid-liquid separation, thereby obtaining the liquor comprising the at least one rare earth element.

[0135] For example, after the removal of the precipitated Fe_2O_3 , the liquor containing the at least one rare earth element is recirculated back for being further concentrated by being used in precipitating the at least one aluminum ion.

[0136] For example, after the removal of the precipitated Fe_2O_3 , the liquor containing the at least one rare earth element is recirculated back for being further concentrated by being used in precipitating the at least one aluminum ion under the form of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$.

[0137] For example, the at least one iron ion can be Fe^{3+} and it can be substantially selectively partially removed from the composition, and wherein the composition can be further treated with a reducing agent so as to convert Fe^{3+} into Fe^{2+} and then, Fe^{2+} , under the form of FeCl_2 , can be removed from the composition by carrying out a solid-liquid separation, thereby obtaining the liquor comprising the at least one rare earth element.

[0138] For example, the at least one rare earth element can be substantially selectively precipitated, extracted and/or isolated from the liquor by means of a liquid-liquid extraction.

[0139] For example, the at least one rare earth element can be extracted from the liquor by means of liquid-liquid extraction.

[0140] For example, the at least one rare earth element can be recovered from the liquor by means of liquid-liquid extraction.

[0141] For example, the at least one extracting agent can be chosen from di-(2-ethylhexyl) phosphoric acid (HDEHP), mono(2-ethylhexyl)2-ethylhexyl phosphonate (HEH/EHP), bis(2,4,4-trimethylpentyl)monothiophosphinic acid), octyl phenyl phosphate (OPAP), 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (PC88A) and optionally toluene, tributyl phosphate, di-isoamylmethyl phosphonate, 7-(4-ethyl-1-methyloctyl)-8-hydroxyquinoline, di-(2-ethylhexyl) phosphinic acid, bis(2,4,4-trimethylpentyl) phosphinic acid, 8-hydroxyquinoline, and (2-ethylhexyl)phosphonic acid, and mixtures thereof.

[0142] For example, the at least one extracting agent can be di-(2-ethylhexyl) phosphoric acid.

[0143] For example, the at least one extracting agent can be 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester.

[0144] For example, the at least one extracting agent can be octyl phenyl phosphate.

[0145] For example, the at least one extracting agent can be tributyl phosphate.

[0146] For example, the at least one extracting agent can be chosen from diethylenetriamine-pentaacetic acid (DTPA), ethylenediaminetetraacetic (EDTA), 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid (DOTA), bis(2,4,4-trimethylpentyl)monothiophosphinic acid and mixtures thereof.

[0147] According to one example, when substantially selectively precipitating, extracting and/or isolating the at least one rare earth element from the leachate and/or the precipitate, the at least one rare earth element found as an ion in the leachate can be precipitated.

[0148] For example, scandium can be precipitated in the form of $\text{Sc}(\text{OH})_3$, ScCl_3 , ScF_3 , and/or $[\text{ScF}_6]^{3-}$ (cation), wherein the cation can be sodium, potassium, magnesium, calcium etc

[0149] Scandium can be precipitated at a pH of about 7 to about 9, or about 7 to about 8.

[0150] For example, the leaching can be carried out at a pH of about 0.5 to about 2.5, about 0.5 to about 1.5, or about 1; then the second metal ion can be precipitated at a pH of at least about 9.5, 10, 10.5, 11, or 11.5; and then the first metal ion can be precipitated at a pH of about 8 to about 9.

[0151] For example, the second metal ion can be precipitated at a pH of about 10 to about 12.5, 10.5 to about 11.5, about 10.8 to about 11.2, about 11.5 to about 12.5, or between 10 and 11.

[0152] For example, the precipitation of the first metal ion can be carried out at a pH of about 7 to about 11, about 8 to about 10.5, about 8.5 to 10 or about 9 to about 10.

[0153] For example, the precipitation of the second metal ion can be carried out at a pH of about 3 to about 6, about 3.0 to about 5.5, about 3 to about 5, about 3 to about 4, about 3.0 to about 3.5, about 3.5 to about 4.0, about 4.0 to about 5.0, about 4.0 to about 4.5, or about 4.5 to about 5.0.

[0154] For example, the precipitation of the first metal ion can be carried out at a pH of about 5 to about 6, about 5.0 to about 5.5, or about 5.5 to about 6.0.

[0155] For example, when precipitating AlCl_3 , highly concentrated dry gaseous HCl at about 90 to about 98% can be

bubbled into the composition comprising the at least one iron ion, the at least one aluminum ion and the at least one rare earth element.

[0156] For example, when carrying out the hydrolysis of the at least one iron ion so as to convert the at least one iron ion into Fe_2O_3 and removing the Fe_2O_3 , the pH during the hydrolysis can be about below 2.5, 2.0, 1.5 or 1.0.

[0157] According to another example, the liquor can comprise the at least one rare earth element under the form of a chloride, and wherein the liquor can be reacted with an extracting agent in order to substantially selectively extract gallium therefrom, thereby obtaining a Ga-free solution and an extracted gallium solution, and separating the solutions from one another. For example, gallium in the liquor can be under the form of GaCl_3 . For example, the extracting agent can be octyl phenyl phosphate, 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester and toluene, tri-butyl phosphate or mixtures thereof. For example, the extracted GaCl_3 can then be precipitated and then converted into Ga_2O_3 . The latter can be further processed through a plasma torch for purification above 99.5%.

[0158] For example, the Ga-free solution can then be reacted with another an extracting agent in order to substantially selectively extract cerium therefrom, thereby obtaining a Ce-free solution and an extracted cerium solution, and separating the solutions from one another. For example, the cerium in the Ga-free solution can be under the form of CeCl_3 . For example, the another extracting agent can be tri-butyl phosphate, di-isoamylmethyl phosphonate, di-(2-ethylhexyl) phosphoric acid, 7-(4-ethyl-1-methyloctyl)-8-hydroxyquinoline or mixtures thereof. For example, the process can further comprise converting the extracted cerium into Ce_2O_3 . For example, the extracted cerium can be calcinated into Ce_2O_3 . If the extracted cerium in under the form of a chloride, HCl can be recovered (or regenerated) from such a calcination process. For example, HCl can be regenerated at its azeotropic concentration.

[0159] For example, the process can further comprise reacting the Ce-free solution with a further extracting agent in order to substantially selectively extract scandium therefrom, thereby obtaining a Sc-free solution and an extracted scandium solution, and separating the solutions from one another. For example, scandium in the Ce-free solution. can be under the form of ScCl_3 . For example, the further extracting agent can be di-(2-ethylhexyl) phosphoric acid, di-(2-ethylhexyl) phosphinic acid or a mixture thereof. For example, the process can further comprise converting the extracted scandium into Sc_2O_3 . For example the extracted scandium can be converted into Sc_2O_3 by means of NaOH. The extracted scandium can be calcined so as to obtain Sc_2O_3 . If the extracted scandium is under the form of a chloride, HCl can be recovered (or regenerated) from such a calcination process. For example, HCl can be regenerated at its azeotropic concentration.

[0160] For example, the process can further comprise reacting the Sc-free solution with still a further extracting agent in order to substantially selectively extract samarium, europium or a mixture thereof, thereby obtaining a Sm-free solution and/or Eu-free solution and extracted samarium and/or europium solution, and separating the solutions from one another. For example, the still a further extracting agent can be chosen from bis(2,4,4-trimethylpentyl) phosphinic acid, di-(2-ethylhexyl) phosphoric acid and a mixture thereof.

[0161] For example, the process can further comprise reacting the Sm-free solution and/or Eu-free solution with still another extracting agent in order to substantially selectively extract gadolinium, thereby obtaining a Gd-free solution and an extracted gadolinium solution, and separating the solutions from one another. For example, the still another extracting agent can be 8-hydroxyquinoline.

[0162] For example, the process can further comprise reacting the Gd-free solution with yet another extracting agent in order to substantially selectively extract yttrium, thereby obtaining a Y-free solution and an extracted yttrium solution, and separating the solutions from one another. For example, the yet another extracting agent can be (2-ethylhexyl)phosphonic acid, di-(2-ethylhexyl)phosphonic acid or a mixture thereof.

[0163] For example, the process can further comprise reacting the Y-free solution with still yet another extracting agent in order to substantially selectively extract dysprosium and/or erbium, thereby obtaining a Dy-free solution and/or an Er-free solution and an extracted dysprosium and/or erbium solution, and separating the solutions from one another.

[0164] According to another example, the liquor can be reacted with a first extracting agent in order to substantially selectively extract gallium therefrom, thereby obtaining a Ga-free solution and an extracted gallium solution, and separating the solutions from one another.

[0165] For example, gallium in the liquor can be under the form of GaCl_3 . For example, the first extracting agent can be tri-butyl phosphate optionally in kerosene.

[0166] For example, the Ga-free solution can be reacted with a precipitating agent for precipitating at least one rare earth element present in the Ga-free solution, thereby obtaining a precipitate containing the at least one rare earth element and recovering the precipitate via a solid-liquid separation.

[0167] For example, the process can further comprise leaching the precipitate with at least one acid so as to obtain a leach solution comprising the at least one rare earth element. For example the acid can be HCl. For example, the leach solution can be reacted with a second extracting agent so as to substantially selectively extract a first group of rare earth elements, thereby obtaining a solution comprising the extracted rare earth elements of the first group and a raffinate comprising a second group of rare earth elements, and separating the solution from the raffinate. For example, the first group can comprise yttrium and scandium. For example, the second group can comprise cerium, neodymium, europium and praseodymium. For example, the second extracting agent can be chosen from di-(2-ethylhexyl)phosphoric acid and 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester.

[0168] For example, the process can further comprise reacting the solution comprising the extracted rare earth elements of the first group with HCl at least once so as to remove impurities therefrom. For example, HCl can be at azeotropic concentration or it can be a very high concentration such as 95 wt %.

[0169] For example, the process can further comprise stripping the solution comprising the extracted rare earth elements of the first group with at least one acid so as to obtain a first group strip liquor. For example, the at least one acid can be HCl.

[0170] For example, the process can further comprise repeating at least once the extraction with the second extracting agent.

[0171] For example, the first group strip liquor can be reacted with a third extracting agent so as to substantially selectively extracting at least one of scandium, erbium and dysprosium from the first group strip liquor, thereby obtaining a solution comprising the extracted at least one of scandium, erbium and dysprosium, and an yttrium raffinate, and separating the solution from the raffinate. For example, the third extracting agent can be tri-butyl phosphate.

[0172] For example, the process can further comprise stripping the solution comprising the extracted at least one of scandium, erbium and dysprosium solution with at least one acid so as to obtain another first group strip liquor. For example, the at least one acid can be HCl.

[0173] For example, the another first group strip liquor can be reacted with a fourth extracting agent so as to substantially selectively extracting erbium and dysprosium from the another first group strip liquor, thereby obtaining a solution comprising the extracted erbium and dysprosium, and a scandium raffinate, and separating the solution from the raffinate.

[0174] For example, the another first group strip liquor can be reacted with a fourth extracting agent so as to substantially selectively extracting scandium from the another first group strip liquor, thereby obtaining a solution comprising the extracted scandium, and raffinate comprising erbium and dysprosium, and separating the solution from the raffinate.

[0175] For example, the at least one rare earth element can be substantially selectively precipitated, extracted and/or isolated by means of an adsorption on activated charcoal optionally modified with tributyl phosphate or on a polyurethane polyether foam (PUF).

[0176] For example, the at least one rare earth element can be substantially selectively removed by means of a liquid-liquid extraction. For example, the liquid-liquid extraction can be carried out by using an extracting agent.

[0177] For example, the process can comprise selectively precipitating at least two members chosen from the at least one rare earth element that is in the form of ions, the second metal ion and the first metal ion. For example, each of the members can be precipitated separately or together.

[0178] According to another example, the processes can comprise:

[0179] leaching the at least one material with HCl so as to obtain the leachate comprising a first metal ion a second metal ion and the at least one rare earth element, and the solid and separating the leachate from the solid;

[0180] substantially selectively removing the second metal ion from the leachate, thereby obtaining a composition comprising the first metal ion, and the at least one rare earth element; and

[0181] substantially selectively at least partially removing the first metal ion from the composition, thereby obtaining a liquor comprising the at least one rare earth element.

[0182] According to another example, the processes can comprise:

[0183] leaching the at least one material with HCl so as to obtain the leachate comprising a first metal ion, a second metal ion, and the at least one rare earth element, and the solid and separating the leachate from the solid;

[0184] substantially selectively removing the second metal ion from the leachate, thereby obtaining a composition comprising the first metal ion, and the at least one rare earth element; and

[0185] substantially selectively at least partially removing the first metal ion from the composition, thereby obtaining a liquor comprising the at least one rare earth element.

[0186] According to another example, the leaching can be carried out at a pH of about 0.5 to about 2.5, then the second metal ion can be precipitated at a pH of at least about 9.5, then the first metal ion can be precipitated at a pH of about 8 to about 9, and then at least one scandium ion can be precipitated at a pH of about 7 to about 8.

[0187] According to another example, the leaching can be carried out at a pH of about 0.5 to about 1.5, then the second metal ion can be precipitated at a pH of at least about 10.5, then the first metal ion can be precipitated at a pH of about 8 to about 9, and then at least one scandium ion can be precipitated at a pH of about 7 to about 8.

[0188] According to another example, the leaching can be carried out at a pH of about 0.5 to about 1.5, then the second metal ion can be precipitated at a pH of at least about 11, then the first metal ion can be precipitated at a pH of about 8 to about 9, and then at least one scandium ion can be precipitated at a pH of about 7 to about 8.

[0189] For example, scandium can be precipitated from a by-product generated during the process.

[0190] For example, scandium can be precipitated from a solution generated during the process. For example, scandium can be precipitated using HNO_3 .

[0191] For example, the at least one rare earth element can be substantially selectively precipitated, extracted and/or isolated by at least one technique chosen from ion exchange resin, extraction by means of solvent(s) and adsorption.

[0192] For example, the at least one rare earth element can be substantially selectively precipitated, extracted and/or isolated by means of an ion exchange resin.

[0193] For example, the at least one rare earth element can be substantially selectively precipitated, extracted and/or isolated by means of a liquid-liquid extraction.

[0194] For example, the at least one rare earth element can be substantially selectively precipitated, extracted and/or isolated by means of an electrowinning process.

[0195] According to another example, the leaching can be carried out at a pH of about 0.5 to about 2.5, then the second metal ion can be precipitated at a pH of at least about 9.5, then the first metal ion can be precipitated at a pH of about 8 to about 9, and then and then the at least one rare earth element can be substantially selectively extracted.

[0196] According to another example, the leaching can be carried out at a pH of about 0.5 to about 1.5, then the second metal ion can be precipitated at a pH of at least about 10.5, then the first metal ion can be precipitated at a pH of about 8 to about 9, and then the at least one rare earth element can be substantially selectively extracted.

[0197] According to another example, the leaching can be carried out at a pH of about 0.5 to about 1.5, then the second metal ion can be precipitated at a pH of at least about 11, then the first metal ion can be precipitated at a pH of about 8 to about 9, and then the at least one rare earth element can be substantially selectively extracted.

[0198] For example, the at least one material/acid ratio can be about $\frac{1}{10}$ in weight by volume.

[0199] According to another example, the processes can further comprise at least one of

[0200] at least partially removing the second metal ion from the leachate by substantially complexing the second metal ion with an extracting agent;

[0201] selectively precipitating the second metal ion;

[0202] selectively precipitating the first metal ion; and

[0203] at least partially removing the first metal ion from the leachate by substantially complexing the first metal ion with another extracting agent.

[0204] According to another example, the processes comprise:

[0205] leaching the at least one material with HCl so as to obtain a leachate comprising a first metal ion and a second metal ion and a solid residue, and separating the leachate from the solid residue;

[0206] at least partially removing the second metal ion from the leachate by substantially selectively precipitating the second metal ion by reacting the leachate with a base so as to obtain an aqueous composition rich in the first metal ion and comprising the at least one rare element and a precipitate, and removing the precipitate from the composition;

[0207] purifying the aqueous composition by substantially selectively precipitating the first metal ion, thereby obtaining another composition comprising the at least one rare element and another precipitate, removing the precipitate from the composition; and

[0208] substantially selectively extracting the at least one rare element from the another composition.

[0209] According to another example, the processes can comprise:

[0210] leaching the at least one material with HCl so as to obtain a leachate comprising a first metal ion and a second metal ion and a solid residue, and separating the leachate from the solid residue,

[0211] at least partially removing the second metal ion from the leachate by substantially selectively precipitating the second metal ion by reacting the leachate with a base so as to obtain an aqueous composition rich in the first metal ion and comprising the at least one rare element and a precipitate, and removing the precipitate from the composition;

[0212] substantially selectively extracting the first metal ion from the aqueous composition by means of a hollow fiber membrane, or by a liquid-liquid extraction, and removing the extracted first metal ion, thereby obtaining an aqueous composition depleted in the first metal ion comprising the at least one rare element; and

[0213] substantially selectively extracting the at least one rare element from the aqueous composition.

[0214] According to another example, the processes can comprise:

[0215] leaching the at least one material with HCl so as to obtain a leachate comprising a first metal ion and a second metal ion and a solid residue, and separating the leachate from the solid residue;

[0216] at least partially removing the second metal ion from the leachate by substantially selectively complexing the second metal ion with an extracting agent so as to obtain an aqueous composition rich in the first metal ion comprising the at least one rare earth element;

[0217] purifying the aqueous composition by substantially selectively precipitating the first metal ion, thereby obtaining another composition comprising the at least one rare element and another precipitate, removing the precipitate from the composition; and

[0218] substantially selectively extracting the at least one rare element from the another composition.

[0219] According to another example, the processes can comprise:

[0220] leaching the at least one material with HCl so as to obtain a leachate comprising a first metal ion and a second metal ion and a solid residue, and separating the leachate from the solid residue;

[0221] at least partially removing the second metal ion from the leachate by substantially selectively complexing the

second metal ion with an extracting agent so as to obtain an aqueous composition rich in the first metal ion comprising the at least one rare earth element;

[0222] substantially selectively extracting the first metal ion from the aqueous composition by means of a hollow fiber membrane, or by a liquid-liquid extraction, and removing the extracted first metal ion, thereby obtaining an aqueous composition depleted in the first metal ion comprising the at least one rare element; and

[0223] substantially selectively extracting the at least one rare element from the aqueous composition depleted in the first metal ion.

[0224] According to another example, the processes can comprise:

[0225] leaching the at least one material with HCl so as to obtain a leachate comprising a first metal ion and a second metal ion and a solid residue, and separating the leachate from the solid residue;

[0226] at least partially removing the first metal ion from the leachate by substantially selectively precipitating the first metal ion so as to obtain an aqueous composition rich in the second metal ion comprising the at least one rare element and a precipitate, and removing the precipitate from the composition;

[0227] substantially selectively precipitating the second metal ion from the aqueous composition rich in the second metal ion, and removing the precipitate therefrom, thereby obtaining thereby obtaining an aqueous composition depleted in the second metal ion and comprising the at least one rare element; and

[0228] substantially selectively extracting the at least one rare element from the aqueous composition depleted in the second metal ion.

[0229] For example, the first metal ion can comprises at least one aluminum ion.

[0230] For example, the second metal ion can comprise at least one iron ion.

[0231] For example, the at least one aluminum ion can be precipitated under the form of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ in a crystallizer, for example, by sparging gaseous HCl.

[0232] For example, the at least one aluminum ion can be precipitated under the form of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ in a crystallizer, for example, by adding HCl having a concentration of about 26 to about 32 wt %.

[0233] For example, the at least one iron ion can be precipitated under the form of Fe_2O_3 by means, for example, of an hydrolysis.

[0234] For example, the aqueous composition rich in the first metal ion can be purified by complexing the first metal ion with an extracting agent so as to obtain a complex, separating the complex form the composition and precipitating the first metal ion.

[0235] For example, the aqueous composition rich in the first metal ion can be purified by complexing impurities contained in aqueous composition rich in the first metal ion with an extracting agent, at least partially removing the complexed impurities from the composition and precipitating the first metal ion.

[0236] For example, the rare earth elements and rare metals obtained by the processes of the present disclosure can be further purified by means of a plasma torch. For example, the rare earth elements and rare metals, once isolated, can be individually injected into a plasma torch so as to further

purify them. Examples of such optional purification steps can be seen in FIGS. 4C, 4D, 5F, 5G and 5H.

[0237] For example, the acidic compositions of the present disclosure can be treated by means of an ion exchange resin prior to extraction of the at least one rare earth element and/or at least rare metal. Examples of such steps can be seen, for example, in FIGS. 3A, 4C, 5E and 5F.

[0238] For example, the acidic composition can be reacted with $\text{Fe}(0)$, thereby obtaining a composition having a reduced content in Fe^{3+} .

[0239] For example, the first rare earth element can be scandium.

[0240] For example, the acidic composition can comprise at least one rare metal.

[0241] For example, the processes can comprise reacting the composition having the reduced content in the at least one iron ion with the precipitating agent so as to substantially selectively precipitate the first rare earth element and the first rare metal.

[0242] For example, the first rare metal can be gallium.

[0243] For example, the precipitating agent can be chosen from oxalic acid, NaOH , MgO , CaCO_3 and mixtures thereof.

[0244] For example, the precipitating agent can be CaCO_3 .

[0245] For example, the first rare earth element and optionally the first rare metal is/are substantially selectively precipitated by maintaining a pH value below 2, or a pH at a value of about 1 to about 2.

[0246] For example, the first rare earth element and optionally the first rare metal is/are substantially selectively precipitated by maintaining Redox potential of about +380 mV.

[0247] For example, the processes can comprise reacting the composition having reduced content in the at least one iron ion with the precipitating agent so as to substantially selectively precipitate a first rare earth element and first rare metal that are comprised in a so-formed precipitate, and recovering the precipitate.

[0248] For example, the processes can further comprising leaching the precipitate and obtaining a leaching solution.

[0249] For example, the precipitate can be leached with HCl .

[0250] For example, HCl can have a concentration of about 5 to about 15 mol/L.

[0251] For example, the leaching solution can be further extracted with an extracting agent so as to substantially selectively extract the first rare earth element and the first rare metal and obtain a loaded organic phase.

[0252] For example, the extracting agent can be tri-butyl phosphate, tri-butyl phosphate in kerosene or tri-butyl phosphate in kerosene and in the presence of isodecanol.

[0253] For example, the processes can further comprising scrubbing the loaded organic phase with a scrubbing solution so as to recover the first rare earth element and obtained a scrubbed organic phase.

[0254] For example, the scrubbing solution can be an acidic aqueous solution comprising HCl at a concentration of about 2 to about 12 mol/L.

[0255] For example, the scrubbing solution can be used in a ratio scrubbing solution:loaded organic phase of about 1:1.

[0256] For example, the processes can further comprise stripping the scrubbed organic phase with a stripping solution so as to recover the first rare metal.

[0257] For example, the stripping solution can be water.

[0258] For example, the stripping solution can be used in a ratio stripping solution:loaded organic phase of about 1:2.

[0259] For example, the composition having a reduced content in the at least one iron ion can be reacted with the precipitating agent so as to obtain a liquid comprising at least one further rare earth element and the precipitate comprising the first rare earth element and the first rare metal, the process further comprising separating the liquid from the precipitate.

[0260] For example, the process can further comprise reacting the liquid with another precipitating agent so as to obtain another precipitate, and recovering the another precipitate.

[0261] For example, the liquid can be reacted with the another precipitating agent at a pH of about 7.8 to about 8.2 or about 7.9 to about 8.1.

[0262] For example, the liquid can be reacted with the another precipitating agent by maintaining Redox potential at about +340 mV or at about +380 mV.

[0263] For example, the liquid can be reacted with the another precipitating agent by maintaining a temperature of about 50 to about 70° C.

[0264] For example, the another precipitating agent can be chosen from oxalic acid, NaOH , MgO , CaCO_3 and mixtures thereof.

[0265] For example, the another precipitating agent can be CaCO_3 .

[0266] For example, the processes can further comprise leaching the another precipitate and obtaining a leaching solution comprising a second rare earth element.

[0267] For example, the another precipitate can be leached with HCl .

[0268] For example, the leaching solution comprising the second rare earth element can be extracted with an extracting agent so as to substantially selectively extract the second rare earth element and obtain a loaded organic phase comprising the second rare earth element and an aqueous phase comprising at least one light rare earth element.

[0269] For example, the extracting agent di(ethylhexyl) phosphonic acid or di(ethylhexyl)phosphonic acid in kerosene.

[0270] For example, the processes can further comprise at least partially removing a third rare earth element from the loaded organic phase comprising the second rare earth element.

[0271] For example, the processes can further comprise at least partially removing a third rare earth element from the loaded organic phase comprising the second rare earth element by treating the loaded organic phase with an acidic scrubbing solution. For example, the scrubbing solution can comprise 1 N HCl .

[0272] For example, the third rare earth element can cerium.

[0273] For example, the processes can further comprise treating the loaded organic phase comprising the second rare earth element with an acidic stripping solution so as to obtain a strip liquor comprising the second rare earth element and recovering the strip liquor. For example, the strip liquor can comprise 3.5 N HCl .

[0274] For example, the processes can comprise treating the strip liquor comprising the second rare earth element with an extracting agent so as to substantially selectively extract a fourth rare earth element and optionally a fifth rare earth element from the strip liquor and obtaining a raffinate comprising the second rare earth element. For example, the extracting agent can be tri-butyl phosphate or tri-butyl phosphate in kerosene.

[0275] For example, the fourth rare earth element can be dysprosium.

[0276] For example, the fifth rare earth element is erbium.

[0277] For example, the processes can further comprise reacting an organic phase comprising the fourth rare earth element and optionally the fifth rare earth element with a strip solution so as to obtain a strip liquor comprising the fifth rare earth element and optionally the fifth rare earth element. For example, the strip solution can be water.

[0278] For example, the second rare earth element is yttrium.

[0279] For example, the leaching solution comprising the second rare earth element can be extracted with an extracting agent so as to substantially selectively extract the second rare earth element and obtain a loaded organic phase comprising the second rare earth element and a raffinate comprising at least one light rare earth element. For example, the extracting agent can be di(ethylhexyl)phosphonic acid or di-(2-ethylhexyl) phosphoric acid.

[0280] For example, the processes can further comprise at least partially removing a third rare earth element from the loaded organic phase comprising the second rare earth element.

[0281] For example, the processes can further comprise at least partially removing a third rare earth element from the loaded organic phase comprising the second rare earth element by treating the loaded organic phase with an acidic scrubbing solution. For example, the scrubbing solution comprises about 1 N to about 2 N HCl.

[0282] For example, the processes can further comprise treating the loaded organic phase comprising the second rare earth element with a stripping solution so as to obtain a strip liquor comprising the second rare earth element. The stripping solution can comprise about 3 M to about 4M HCl.

[0283] For example, the strip liquor comprising the second rare earth element can be extracted with an extracting agent so as to remove a fourth rare earth element and optionally a fifth rare earth element, thereby obtaining a raffinate comprising the second rare earth element and a loaded organic phase comprising the fourth rare earth element and optionally the fifth rare earth element. For example, the extracting agent is tri-butyl phosphate or tri-butyl phosphate in kerosene.

[0284] For example, the processes can comprise recovering the raffinate comprising the second rare earth element.

[0285] For example, the second rare earth element can be yttrium.

[0286] For example, the fourth rare earth element can be dysprosium.

[0287] For example, the fifth rare earth element can be erbium.

[0288] For example, the processes can further comprise reacting the loaded organic phase comprising the fourth rare earth element and the fifth rare earth element with a stripping solution so as to obtain strip liquor comprising the fourth rare earth element and the fifth rare earth element. For example, the stripping solution can be water.

[0289] For example, the processes can further comprise reacting the strip liquor with an extracting agent so as to substantially selectively extract the fifth rare earth element from the strip liquor, thereby obtaining a raffinate comprising the fourth rare earth element and a loaded organic phase comprising the fifth rare earth element. For example, the extracting agent can be di(ethylhexyl)phosphonic acid or di-(2-ethylhexyl) phosphoric acid.

[0290] For example, the processes can further comprise separating the raffinate from the loaded organic phase comprising the fifth rare earth element, treating the loaded organic phase with a scrubbing solution so as to remove impurities therefrom and then treating the loaded organic phase with a stripping solution so as to obtain a strip liquor comprising the fifth rare earth element. For example, the scrubbing solution can comprise about 2 M to about 4 M HCl.

[0291] For example, the raffinate can be reacted with an oxidation agent so as to oxidize the third rare earth element. For example, the oxidation agent can comprise sodium hypochlorite. For example, the raffinate can be reacted with an oxidation agent at a pH of about 0.5 to about 1.5.

[0292] For example, the processes can further comprise removing, from the raffinate, the oxidized third rare earth element that is under the form of a precipitate, thereby obtaining a filtrate comprising a sixth rare earth element.

[0293] For example, the processes can further comprise reacting the filtrate with an extracting agent so as to substantially selectively extracting the sixth rare earth element from the filtrate, thereby obtaining a loaded organic phase comprising the sixth rare earth element and another raffinate comprising a seventh rare earth element and an eight rare earth element, and separating the loaded organic phase comprising the sixth rare earth element from the raffinate. For example, the extracting agent can be di(ethylhexyl)phosphonic acid or di-(2-ethylhexyl) phosphoric acid.

[0294] For example, the processes can further comprise treating the loaded organic phase with a scrubbing solution so as to remove impurities therefrom and then treating the loaded organic phase with a stripping solution so as to obtain a strip liquor comprising the sixth rare earth element. For example, the scrubbing solution can comprise about 0.5 M to about 1.5 M HCl. For example, the stripping solution can comprise about 2 M to about 3 M HCl.

[0295] For example, the sixth rare earth element can europium.

[0296] For example, the seventh rare earth element can be praseodymium.

[0297] For example, the eighth rare earth element can be neodymium.

[0298] For example, the processes can further comprise reducing the sixth rare earth element by means of a reducing agent. For example, the reducing agent can be zinc (0).

[0299] For example, the processes can further comprise reacting the sixth rare earth element with sodium sulphate so as to obtain a sulphate derivative thereof under the form of a precipitate and recovering the precipitate.

[0300] For example, the processes can further comprise reacting the raffinate comprising the seventh rare earth element and the eight rare earth element with an extracting agent so as to substantially selectively extracting the eight rare earth element from the raffinate, thereby obtaining a loaded organic phase comprising the eight rare earth element a raffinate comprising the seventh rare earth element, and separating the loaded organic phase comprising the eight rare earth element from the raffinate. For example, the extracting agent can be di(ethylhexyl)phosphonic acid or di-(2-ethylhexyl) phosphoric acid.

[0301] For example, the processes can further comprise treating the loaded organic phase with a scrubbing solution so as to remove impurities therefrom and then treating the loaded organic phase with a stripping solution so as to obtain a strip liquor comprising the eight rare earth element. For

example the scrubbing solution can comprise about 2 M to about 3 M HCl. For example, the stripping solution can comprise about 3 M to about 4 M HCl.

[0302] For example, the processes can further comprise, pre-treating or treating the acidic composition with an ion exchange resin so as to remove impurities.

[0303] For example, the processes can further comprise, before extracting at least one rare earth element and optionally at least one rare metal from the acidic composition, treating the acidic composition with an ion exchange resin so as to at least partially remove impurities therefrom.

[0304] For example, the processes can further comprise treating the at least one rare earth element and optionally the at least one rare metal extracted by the process by means of a plasma torch so as to further purify the at least one rare earth element and optionally the at least one rare metal.

[0305] According to another example the processes can comprise:

[0306] 1—leaching argillite with at least one acid (for example a solution of HCl or gaseous HCl (for example at pH of about 0.5 to about 1.5 or about 0.8 to about 1.2). The leaching can also be carried out under pressure;

[0307] 2—removing iron by ionic precipitation by raising pH at pH of about 10 to about 12 or about 11 to about 12 (or extracting it with extracting agents) and filtering out all non-soluble hydroxides;

[0308] 3—precipitating aluminum at a pH of about 7.5 to about 9.0 or about 7.8 to about 8.2 and filtering aluminium hydroxide as a solid;

[0309] 4—optionally purifying aluminum ($\text{Al}(\text{OH})_3$) using at least one of a liquid-liquid extraction, a membrane and an extracting agent suitable for complexing aluminum ions; and

[0310] 5—precipitating, extracting and/or isolating at least one rare earth element can be carried out after at least one of steps 1, 2, 3 and 4.

[0311] For more details and explanations regarding at least certain portions of steps 1 to 4, WO2008141423, which is hereby incorporated by reference in its entirety, can be referred to.

[0312] According to another example the processes can comprise:

[0313] 1—leaching argillite with an acid (for example a solution of HCl 18-32 wt %. The leaching can also be carried out under pressure such as about 350 KPag to about 500 KPag during about 4 to about 7 hours;

[0314] 2—removing iron by ionic precipitation by raising the pH at pH of about 10 to about 12 or about 11 to about 12 (or extracting it with extracting agents) and filtering out all non-soluble hydroxides;

[0315] 3—precipitating aluminum at a pH of about 7.5 to about 9.0 or about 7.8 to about 8.2 and filtering aluminium hydroxide as a solid;

[0316] 4—optionally purifying aluminum ($\text{Al}(\text{OH})_3$) using at least one of a liquid-liquid extraction, a membrane and an extracting agent suitable for complexing aluminum ions; and

[0317] 5—precipitating, extracting and/or isolating at least one rare earth element can be carried out after at least one of steps 1, 2, 3 and 4.

[0318] According to another example as shown in FIG. 1, the processes can involve the following steps (the reference numbers in FIG. 1 correspond to the following steps):

[0319] 1—The aluminum-containing material is reduced to an average particle size of about 50 to about 80 μm .

[0320] 2—The reduced and classified material is treated with hydrochloric acid which allows for dissolving, under a predetermined temperature and pressure, the aluminum with other elements like iron, magnesium and other metals including rare earth. The silica (and optionally titanium) remains totally undissolved.

[0321] 3—The mother liquor from the leaching step then undergoes a separation, a cleaning stage in order to separate the purified silica from the metal chloride in solution. The purified silica can then undergo one or two additional leaching stages (for example at a temperature of about 150 to about 160° C.) so as to increase the purity of silica above 99.9%. TiO_2 contained in silica can be separated from silica through a leach made by using HCl and MgCl_2 as a lixiviant composition.

[0322] 4—The spent acid (leachate) obtained from step 1 is then brought up in concentration with dry and highly concentrated gaseous hydrogen chloride by sparging this one into a crystallizer. This results into the crystallization of aluminum chloride hexahydrate (precipitate) with a minimum of other impurities. Depending on the concentration of iron chloride at this stage, further crystallization step(s) can be required. The precipitate is then separated from the liquid.

[0323] 5—The aluminum chloride hexahydrate is then calcined (for example by means of a rotary kiln, fluid bed, etc) at high temperature in order to obtain the desired alumina. Highly concentrated gaseous hydrogen chloride is then recovered and excess is brought in aqueous form to the highest concentration possible so as to be used (recycled) in the acid leaching step. Acid can also be directly sent in gas phase to the acid purification stage to increase HCl concentration from about 30 wt % to about 95 wt %. This can be done, for example, during drying stage or distillation.

[0324] 6—Iron chloride, rare earth elements and rare metals (the liquid obtained from step 4) is then pre-concentrated and hydrolyzed at low temperature in view of the Fe_2O_3 (hematite form) extraction and acid recovery from its hydrolysis. All heat recovery from the calcination step (step 5), the leaching part exothermic reaction (step 1) and other section of the process is being recovered into the pre-concentrator.

[0325] 10—After the removal of hematite and internal recirculation to crystallizer, a solution rich in rare earth elements can be processed by using any one of the processes described in the present disclosure for recovering rare earth elements from aluminum-containing materials. For example, the recovered rare earth elements can be in various forms such as oxides, chlorides, hydroxides etc. As previously indicated in the present disclosure, the expression “rare earth element” can also encompass “rare metal” and thus, in step 10, rare metals can also be recovered. For example, rare metals can be under the form of rare metals oxides. Thus, in FIGS. 1 and 2, the step 10 can be, for example, the processes shown in FIG. 3 or in FIGS. 4a and 4b.

Other non-hydrolyzable metal chlorides (Me-Cl) such as MgCl_2 and others then undergo the following steps:

[0326] 7—The solution rich in magnesium chloride and other non-hydrolyzable products at low temperature is then brought up in concentration with dry and highly concentrated gaseous hydrogen chloride by sparging it into a crystallizer. This results into the precipitation of magnesium chloride as an hexahydrate.

[0327] 8—Magnesium chloride hexahydrate is then calcined (either through a rotary kiln, fluid bed, etc.) and hydro-

chloric acid at very high concentration is thus regenerated and brought back to the leaching step.

[0328] 9—Other Me-Cl undergo a standard pyrohydrolysis step where mixed oxides can be produced and hydrochloric acid at the azeotropic point (20.2% wt.) is regenerated.

[0329] For example, the liquid can be concentrated to a concentrated liquid having an iron chloride concentration of at least 26% by weight; and then the iron chloride can be hydrolyzed at a temperature of about 155 to about 350° C. while maintaining a ferric chloride concentration at a level of at least 65% by weight, to generate a composition comprising a liquid and precipitated hematite, and recovering the hematite.

[0330] For example, the liquid can be concentrated to a concentrated liquid having an iron chloride concentration of at least 26% by weight; and then the iron chloride can be hydrolyzed at a temperature of about 155 to about 350° C. while maintaining a ferric chloride concentration at a level of at least 65% by weight, to generate a composition comprising a liquid and precipitated hematite; recovering the hematite; and recovering rare earths from the liquid. For example, the process can further comprise, after recovery of the rare earths, reacting the liquid with HCl so as to cause precipitation of $MgCl_2$, and recovering same.

[0331] As previously indicated, various aluminum-containing materials can be used as starting material of the processes disclosed in the present disclosure. Examples with clays and bauxite have been carried out. However, the person skilled in the art will understand that the continuous processes can handle high percentages of silica (>55%) and impurities as well as relatively low percentages of aluminum (for example as low as about 15%) and still being economically and technically viable. Satisfactory yields can be obtained (>93-95%) on Al_2O_3 and greater than 75%, 85% or 90% on rare earth elements and rare metals. No pre-thermal treatment in most cases are required. The processes disclosed in the present disclosure involve special techniques on leaching and acid recovery at very high strength, thereby offering several advantages over alkaline processes. No solid residues as per alkaline processes are generated by that process which benefits from the totally integrated HCl recovery loop.

[0332] In step 1 the mineral, whether or not thermally treated is crushed, milled, dried and classified to have an average particle size of about 50 to about 80 μm .

[0333] In step 2, the milled raw material is introduced into the reactor and will undergo the leaching phase.

[0334] The leaching hydrochloric acid used in step 2 is a recycled or regenerated acid from steps 5, 6, 8 and 9 and its concentration can vary from 15% to 45% weight. percent. Higher concentration can be obtained using a membrane separation, a cryogenic and/or high pressure approach. The acid leaching can be carried out under pressure and at temperature close to its boiling point thus, allowing a minimal digestion time and extended reaction extent (90%-100%). Leaching (step 2) can be accomplished in a semi-continuous mode where spent acid with residual free hydrochloric acid is replaced by highly concentrated acid at a certain stage of the reaction or allowing a reduced acid/mineral ratio, thereby reducing reaction time and improving reaction kinetics. For example, kinetic constant k can be: 0.5-0.75 g/mole·L, or 0.75-1.10 g/mole·L.

[0335] As previously indicated, alkali metals, iron, magnesium, calcium, potassium, rare earth elements and other elements will also be in a chloride form at different stages. Silica

and titanium can remain undissolved and will undergo (step 3) a liquid/solid separation and cleaning stage. The processes of the present disclosure tend to recover maximum amount of free hydrochloric acid left and chlorides in solution in order to maximize hydrochloric acid recovery yield, using techniques such as rake classifying, filtration with band filters, centrifugation, and others. Mother liquor free of silica is then named as spent acid (various metal chlorides and water) and goes to the crystallization step (step 4).

[0336] In step 4, the spent acid (or leachate) with a substantial amount of aluminum chloride is then saturated with dry and highly concentrated gaseous hydrogen chloride obtained or recycled from step 5, which results in the precipitate of aluminum chloride hexahydrate ($AlCl_3 \cdot 6H_2O$). The precipitate retained is then filtered or centrifuged before being fed to the calcination stage (step 5). The remaining of the spent acid from step 4 is then processed to acid recovery system (steps 6 to 8) where pure secondary products will be obtained.

[0337] In step 5, aluminum oxide (alumina) is directly obtained from high temperature conditions. The highly concentrated hydrogen chloride in gaseous form obtained can be fed to steps 4 and 7 for crystallization. The excess hydrogen chloride is absorbed and used as regenerated acid to the leaching step 2 as highly concentrated acid, higher than the concentration at the azeotropic point (>20.2%). For example, such a concentration can be about 25 to about 45 weight % or between 25 and 36 weight %. Acid can also be redirected in gas phase directly (>30 wt %) to acid purification.

[0338] After step 4, various chlorides derivatives of (mainly iron chlorides, magnesium chloride and rare earth element in the form of chlorides) are next subjected to an iron extraction step. Such a step can be carried out for example by using the technology disclosed in WO 2009/153321, which is hereby incorporated by reference in its entirety. Moreover, hematite can be seeded for crystal growth.

[0339] In step 6, a hydrolysis at low temperature (155-350° C.) is carried out and pure Fe_2O_3 (hematite) is being produced and hydrochloric acid of at least 15% concentration is being regenerated. The method as described in WO 2009/153321 is processing the solution of ferrous chloride and ferric chloride, possible mixtures thereof, and free hydrochloric acid through a series of steps pre-concentration step, oxidation step where ferrous chloride is oxidized into ferric form, and finally through an hydrolysis step into an operational unit called hydrolyser where the ferric chloride concentration is maintained at 65 weight % to generate a rich gas stream where concentration ensures a hydrogen chloride concentration of 15-20.2% and a pure hematite that will undergo a physical separation step. Latent heat of condensation is recovered to the pre-concentration and used as the heating input with excess heat from the calcination stage (step 5).

[0340] The mother liquor left from the hydrolyser (step 6), after iron removal, is rich in other non-hydrolysable elements and mainly comprises magnesium chloride or possible mixture of other elements (various chlorides) and rare earth elements.

[0341] Rare earth elements in form of chlorides are highly concentrated in percentage into the hydrolyser operational unit (step 6) and are extracted from the mother liquor (step 10) where the processes defined in the present disclosure for recovering rare earth elements from aluminum-containing materials can be employed. For example, rare earth elements under various forms can thus be extracted. For example, it can be under the form of oxides. REO. The processes of the

present disclosure for recovering rare earth elements can allow, for example, to concentrate to a high concentration the following rare earth elements, within the hydrolyser recirculation loop: scandium (Sc), gallium (Ga), yttrium (Y), dysprosium (Dy), cerium (Ce), praseodymium (Pr), neodymium (Nd), europium (Eu), samarium (Sm), gadolinium (Gd), lanthanum (La), erbium (Er). Of course, the at least one rare earth element that will be recovered will depend upon the nature of the starting material (aluminum-containing material).

[0342] The spent acid liquor from steps 6 and 10 rich in value added metals, mainly magnesium, is processed to step 7. The solution is saturated with dry and highly concentrated gaseous hydrogen chloride from step 5, which results in the precipitation of magnesium chloride hexahydrate. The precipitate retained, is fed to a calcination stage step 8 where pure MgO (>98% wt.) is obtained and highly concentrated hydrochloric acid (for example of at least 38%) is regenerated and diverted to the leaching step (step 2). An alternative route for step 7 is using dry gaseous hydrochloric acid from step 8.

[0343] In step 9, metal chlorides unconverted are processed to a pyrohydrolysis step (700-900° C.) to generate mixed oxides and where hydrochloric acid from 15-20.2% wt. concentration can be recovered.

[0344] According to another example as shown in FIG. 2, the processes can be similar to the example shown in FIG. 1 but can comprise some variants as below discussed.

[0345] In fact, as shown in FIG. 2, the process can comprise (after step 6 or just before step 10) an internal recirculation back to the crystallization step 4. In such a case, The mother liquor from the hydrolyser (step 6) can be recirculated fully or partially to the crystallization of step 4 where a concentration increase will occur with respect to the non-hydrolyzable elements including rare earth elements.

[0346] Such a step can be useful for significantly increasing the concentration of rare earth elements, thereby facilitating their extraction in step 10.

[0347] With respect to step 7, the solution rich in magnesium chloride and other non-hydrolyzable products at low temperature is, as previously discussed, then brought up in concentration with dry and highly concentrated gaseous hydrogen chloride by sparging it into a crystallizer. This can result into the precipitation of magnesium chloride as an hexahydrate (for example after sodium and potassium chloride removal).

[0348] As shown in FIG. 2, an extra step 11 can be added. Sodium chloride can undergo a chemical reaction with sulfuric acid so as to obtain sodium sulfate and regenerate hydrochloric acid at the azeotropic point. Potassium chloride can undergo a chemical reaction with sulfuric acid so as to obtain potassium sulfate and regenerate hydrochloric acid at the azeotropic point.

[0349] The process shown in FIG. 2A is similar to the process shown in FIG. 2, with the exception of the fact that it comprises an additional step between stage 12 and stage 2 for using the purified acid obtained.

[0350] The process shown in FIG. 2B is similar to the process shown in FIG. 2, with the exception of the fact that it comprises an additional step of SiO₂ purification by separating TiO₂ therefrom and an optional step 5a in which a low temperature decomposition of alumina chloride can be carried out.

[0351] Between steps 6 and 10 and/or steps 7 and 10 in FIGS. 1 and 2, it is possible to further purify the composition comprising rare earth elements and/or rare metals. In fact,

such a composition can be treated with an ion exchange column so as to remove impurities that are not rare earth elements and rare metals. For example, such a composition that comprises chlorides of rare earth elements and/or rare metals will be treated so as to remove impurities such as iron, aluminum or other metals. Then, once the treatment with such columns is done, the earth elements and/or rare metals can be extracted as indicated in the processes of the present disclosure.

[0352] Certain examples are hereby provided in the present disclosure for substantially selectively recovering, precipitating, extracting and/or isolating at least one rare earth element. This can be done, for example from the leachate and/or the precipitate and any other downstream derivatives, solutions, precipitates, compositions or liquors.

[0353] For example, recovering, precipitating, extracting and/or isolating at least one rare earth element can be carried out by:

[0354] precipitating least one rare earth element (for example at a pH of about 6 to about 8, 7 to about 8, or 7 to about 7.5);

[0355] using an ion exchange resin (for example, as described in U.S. Pat. No. 4,816,233 (hereby incorporated by reference in its entirety));

[0356] extraction by means of solvent(s) (for example a liquid-liquid extraction can be carried out using di-(2-ethylhexyl) phosphoric acid (HDEHP (also called DEHPA or D2EHPA)), mono(2-ethylhexyl)2-ethylhexyl phosphonate (HEH/EHP), octyl phenyl phosphate (OPAP), 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (PC88A) and optionally toluene (for example as described in Kao et al. in Chemical Engineering Journal, Volume 119, Issues 2-3, Jun. 15, 2006, pages 167-174 (hereby incorporated by reference in its entirety)) or by means of extracted using an alkyl phosphate (for example as described in U.S. Pat. No. 3,013, 859 (hereby incorporated by reference in its entirety));

[0357] using an extracting agent (for example using bis (2,4,4-trimethylpentyl)monothiophosphinic acid or a derivative thereof);

[0358] adsorption on activated charcoal (activated carbon adsorption) optionally modified with tributyl phosphate or on a polyurethane polyether foam (PUF); (for example as described in Zhou et al. in RARE METALS, Vol. 27, No. 3, 2008, p 223-227 (hereby incorporated by reference in its entirety))

[0359] extraction with hollow fiber membranes; and

[0360] using an electrowinning technology (for example as described in US 2004/0042945 (hereby incorporated by reference in its entirety)).

[0361] For example, scandium can be precipitated (optionally using HNO₃) from a residual solution generated during the process (for example when iron is precipitated and/or when aluminum is precipitated).

[0362] For example, when substantially selectively precipitating, extracting and/or isolating at least one rare earth element from the leachate and/or the precipitate and any other downstream derivatives, various sequences can be carried out i.e. depending on the nature of the starting material and the rare earth elements present, a given rare earth element can be more easily extracted before or after another given rare earth element.

[0363] For example, as shown in FIG. 3, in a mixture or liquor comprising HCl, water and rare elements in the form of

chlorides, the mixture can be treated with an extracting agent in order to extract GaCl_3 therefrom, thereby obtaining a Ga-free solution. Such an extracting agent can be, for example, octyl phenyl phosphate (OPAP) or 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (PC88A) and toluene. GaCl_3 can then be precipitated and then converted into Ga_2O_3 by heating it, while, optionally recovering HCl.

[0364] Then, the Ga-free solution can be treated with an extracting agent (for example SME 529TM, tri-butyl phosphate or di-isoamylmethyl phosphonate, di-(2-ethylhexyl) phosphoric acid, 7-(4-ethyl-1-methyloctyl)-8-hydroxyquinoline (Kelex 100TM) in n-heptane with the addition of 10% n-decanol.) for substantially selectively extracting cerium chloride therefrom so as to obtain a Ce-free solution. CeCl_3 can be eventually converted into Ce_2O_3 , while, optionally recovering HCl.

[0365] Then, the Ce-free solution can be treated with an extracting agent such as di-(2-ethylhexyl) phosphoric acid or di-(2-ethylhexyl) phosphinic acid so as substantially selectively extract Sc and to provide a Sc-free solution. The extracted Sc can be treated with an oxidizer (such as NaOH) so as to provide Sc_2O_3 .

[0366] Then, the various remaining rare earth elements (Pr, Nd, Sm, Eu, La, Gd, Y, Dy, Er etc.) in the Sc-free solution can be extracted in different possible orders.

[0367] For example, it has to be noted that the process schematized in FIG. 3 can be used as a component of various other processes such as the process schematized in FIG. 1 or in FIG. 2. For example, the step 10 of FIGS. 1 and 2 can be the process schematized in FIG. 3.

[0368] The process shown in FIG. 3A is similar to the process shown in FIG. 3, with the exception that it comprises an extra purification step by using an ion exchange column.

[0369] For example, as shown in FIGS. 4A and 4B, the process for extracting rare earth elements can comprise:

[0370] Ferric reduction to ferrous using iron;

[0371] Separation of gallium from the ferrous chloride solution;

[0372] Precipitation and pre-concentration of rare earth elements from the raffinate;

[0373] Re-leaching and fractioning of the rare earth elements into light (LRE) and heavy (HRE) groups;

[0374] Separation of yttrium from scandium and heavy rare earth elements;

[0375] Separation of scandium and heavy rare earth elements; and

[0376] Leaching with low concentration acid at atmospheric pressure

[0377] The processes shown in FIGS. 4C and 4D are similar to the processes shown in FIGS. 4A and 4B, with the exception that they can comprise an extra purification step by using an ion exchange column, an optional plasma purification step, an extra acid regenerations step, and an extra calcination step.

[0378] The reduction of ferric to ferrous with a reducing agent (such as metallic iron, starch) can be used so as to prevent iron coextraction or iron precipitation. The reaction time can be very short and it can generate heat. The general chemical reaction for reduction of iron(III) is shown below.



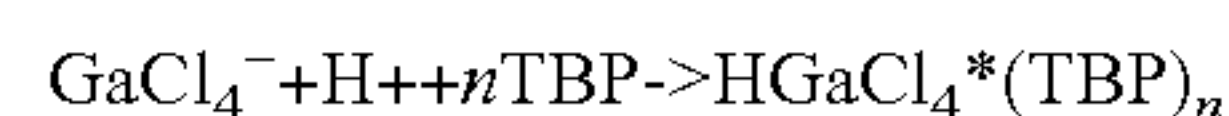
[0379] As long as the feed solution is held under reduced conditions, no ferric will be present in this liquid solution. As shown in FIGS. 4a and 4b, The ferric chloride feed solution

101 can be fed to an agitated reaction tank and a reducing agent (for example metallic iron 102) can added so as to allow for converting ferric chloride to ferrous chloride (see “Ferric Removal”). After a solid-liquid separation (s/l separation), the resulting filtrate 103 can be further treated in a gallium extraction circuit. A filter cake, containing solid material and iron, can be dewatered and the resulting slurry can then be prepared for disposal.

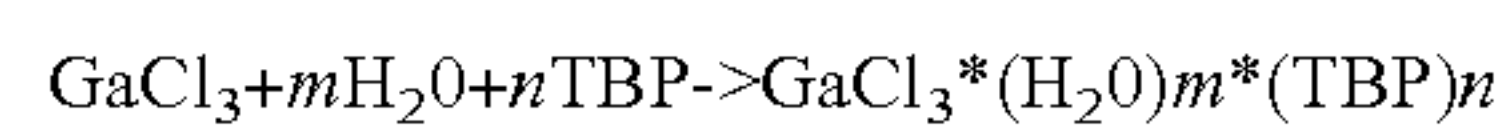
[0380] Gallium can then be extracted with an organic solution containing an extracting agent (for example tri-butyl phosphate (TBP) dissolved in kerosene) (see “Gallium Recovery”). The rare earth elements and iron can thus be left in the raffinate. The extraction can vary as a function of the chloride ion concentration. For example, the higher chloride ion concentration, the stronger tendency for gallium complex formation and the better extraction.

[0381] For example, for gallium (recovery from hydrochloric acid solutions, reagents such as tri-butyl phosphate or tertiary amines (e.g. Alamine 336) can be used. For example, when increasing hydrochloric acid (HCl) concentration, gallium extraction can rise to a maximum and can then decrease again. For example, HCl concentration can be increased up to about 4 M HCl for the gallium extraction. Under these conditions, gallium can be present in the form of HGaCl_4 complex and TBP extracted gallium as a trisolvate ($\text{HGaCl}_4 \cdot 3\text{TBP}$) (for example when the extracting agent is TBP).

[0382] The rise in extraction with increasing acidity is due to the additional formation of HGaCl_4 . The chemical reaction is shown below.



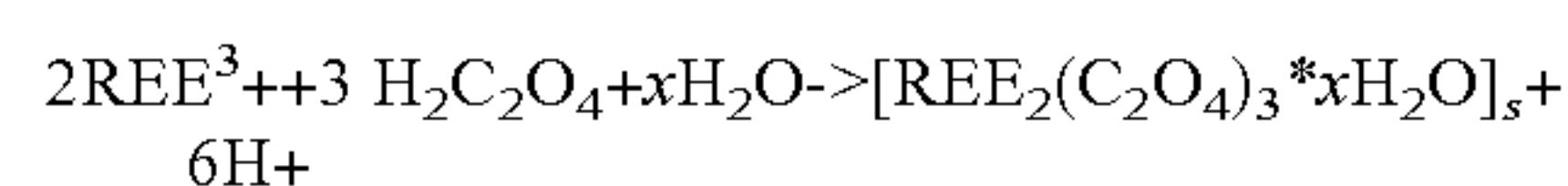
[0383] For low acidity or neutral solutions, the extracted species is GaCl_3 in the form of a hydrated solvate.



[0384] Co-extracted iron, accumulated in the organic phase can be scrubbed with hydrochloric acid (see “Gallium Strip Liquor”). The resulting organic solution, containing gallium can be fed to a stripping circuit where gallium is stripped with water 104. The raffinate 106, containing ferrous chloride and the rare earth elements, can then be fed to the rare earth precipitation section. The final strip liquor 105 contains gallium.

[0385] For example, oxalate precipitation of rare earth elements result in very low solubility of the compounds in aqueous solution. The precipitation of rare earth oxalates can be achieved by addition of a precipitation reagent 107. For example, oxalic acid 107 can be used for the precipitation. For example, precipitating agent that are effective for precipitating rare earth elements of the trivalent (such as oxalate (from oxalic acid)) can be used. For example, such precipitating agents can have provide a very low solubility in aqueous solution to so-formed precipitate.

[0386] The precipitation reaction of trivalent rare earth elements in aqueous solution is according to the following equation:



[0387] An overflow from the primary rare earth elements precipitation 109 can be fed to a ferrous treatment circuit. After filtration, the filter cake, containing the rare earth elements, can be fed to a washing and dewatering unit. A resulting slurry 108 can then be prepared for re-leaching (see

“REE-Re-leaching”). Re-leaching of the rare earth filter cake can be carried out using hydrochloric acid **110**.

[0388] From a pre-concentrated and pH adjusted chloride solution **111**, that contains for example about 150 to about 250 g/L, rare earth elements yttrium, scandium and the heavy rare earth (HRE) are extracted (see “Primary REE Recovery”) with an extracting agent (for example (di-(2-ethylhexyl) phosphoric acid (D2EHPA) or 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (PC88A (also called Ionquest™ 801) in kerosene)). Scandium, the other HRE and also yttrium can be extracted and leaving the light rare earth elements (LRE) in a raffinate **113**.

[0389] A loaded organic phase can then be selectively scrubbed with hydrochloric acid (2 M HCl) to remove the co-extracted LRE. A secondary scrubbing section can remove europium by using weak hydrochloric acid (1 to 1.5 M HCl). The extract, containing yttrium, scandium and the HRE, can then be stripped with strong acid (3.5 M HCl) **112**.

[0390] The HRE strip liquor **114**, containing yttrium and scandium, can be treated further to obtain more than 90% Y_2O_3 and Sc_2O_3 in a first circuit of a double solvent extraction purification process. In a first step, the aqueous solution, containing about 25 g/L (of rare earth elements in the form of oxides) and 0.4 M HCl, can be brought into contact with an extracting agent (for example (di-(2-ethylhexyl)phosphoric acid (D2EHPA) or 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (PC88A (also called Ionquest™ 801) in kerosene)) (see “Secondary REE Recovery”). The loaded organic phase is then scrubbed with diluted hydrochloric acid. Scandium, yttrium and HRE can be extracted by the reagent and finally stripped with strong hydrochloric acid **115** at a high oxide/acid ratio. The final strip liquor would have a concentration in rare earth elements oxides of about 40 g/L and about 1 M HCl. This solution is partially neutralized.

[0391] This pre-treated strip liquor **116** can be further extracted with an extracting agent (for example tri-butyl phosphate (TBP) in kerosene). The treatment can be done in a multi stage procedure, and ending up in a final stripping of the loaded organic with water **117**. All HRE and scandium can thus be extracted, leaving yttrium in a raffinate **119**. A final strip liquor **118**, containing HRE, forms the source for further separation of scandium and heavy rare earth. In order to do so, various possible extracting agents can be used such as di-(2-ethylhexyl) phosphoric acid.

[0392] Yttrium can also be removed from the strip liquor obtained from the primary extraction step. For example, the separation can be carried out at pH 3 after addition of ammonium thiocyanate as complexing reagent. The procedure can result in an yttrium rich raffinate, when extracting heavy rare earth elements with tri-butyl phosphate, Alamine 336 or Aliquat 336.

[0393] The separation of scandium from other HRE, (for example dysprosium and erbium) can be carried out using a further solvent extraction purification circuit, similar to the yttrium separation and purification process and previously described. Thus, the extracting agent can be the same or a different one (for example (di-(2-ethylhexyl)phosphoric acid (D2EHPA); 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (PC88A (also called Ionquest™ 801) in kerosene) or Bis (2,4,4-Trimethylpentyl) Phosphonic acid (Ionquest™ 290)), the strip solution **120** can be the same than **117**, thereby providing a scandium raffinate **121** and a strip liquor **122** comprising europium and erbium.

[0394] As an alternative, yttrium can be extracted as described in U.S. Pat. No. 3,751,553 (hereby incorporated by reference in its entirety). In fact, yttrium can be extracted starting from a xenotime concentrate. It can be done by using three solvent extraction circuits. In a first step, DEHPA can be used to separate yttrium. In a second step, tri (caprylmethyl) ammonium nitrate (Aliquat 336) can be used to extract and separate cerium and leave yttrium in the raffinate. In a third step, Tm, Yb, and Lu can be extracted by means of tri (caprylmethyl) ammonium thio cyanate. In this extraction loop, yttrium behaves like a cerium element. From this step, high-purity of yttrium oxide can be obtained.

[0395] According to another alternative, yttrium oxide can be extracted in two steps i.e. tri (caprylmethyl) ammonium nitrate can be used to separate a mixture La—Er/Y—Lu and then, a purification of yttrium is carried out using versatic acid.

[0396] Solvent extraction is a selective separation procedure for isolating and concentrating valuable elements from an aqueous solution with the aid of an organic solution. In the procedure the aqueous solution containing the element of interest, often at a low concentration and together with other dissolved substances (pollutants), is mixed (extraction) with an organic solvent containing a reagent. The element of interest reacts with the reagent to form a chemical compound that is more soluble in the organic than in the aqueous solution. As a consequence, the element of interest is transferred to the organic solution.

[0397] Subsequently, in order to recover the extracted substance, the organic solution is mixed (stripping) with an aqueous solution whose composition is such that the chemical compound between the element and the reagent is split and, thus, the element is recovered in the “new” aqueous solution, in a pure form. The concentration of the element in the “new” aqueous solution may be increased, often to 10-100 times that of the original aqueous solution, through adjustment of the liquid flow rates. Depleted from the extracted element, the organic solution is returned for further extraction, either directly or after a fraction of it has been cleansed of impurities.

[0398] Important factors that govern this solvent extraction process can be, for example, the number of extraction, scrubbing and stripping stages, organic solvent concentration and diluent.

[0399] In a typical solvent extraction process, the aqueous phase, containing the rare earth elements, can be for example a chloric or nitric acidic solution. The organic phase comprises an extracting agent as those recited in the present disclosure or alternatives in an organic solvent such as an aliphatic diluent.

[0400] Solvent extraction technique can be used as separation and purification procedure for the rare earth elements. Some of the following properties are particularly relevant when selecting an extracting agent or chemical extractant:

[0401] High selectivity over other unwanted metals and acids during the extraction process,

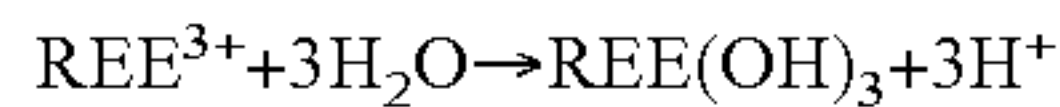
[0402] High transfer capacity on the extractant,

[0403] Good chemical stability,

[0404] Fast kinetics.

[0405] For example, precipitation denotes the removal of the rare earth elements from solution by the addition of a chemical reagent to form a new, less soluble (solid) compound. For example, a complete precipitation can be carried out by oxalate, hydroxide, or other compounds.

[0406] Hydroxide precipitation and double sulphate can also be used. For large scale operation, ammonia can be used for carrying out hydroxide precipitation from nitrate or chloride solutions. The double sulphates $RE_2(SO_4)_3 \cdot Na_2SO_4 \cdot nH_2O$ can be precipitated by either addition of sodium sulphate to the solution containing rare earth elements. The precipitation reaction of trivalent rare earth elements in aqueous solution is according to the following equation:

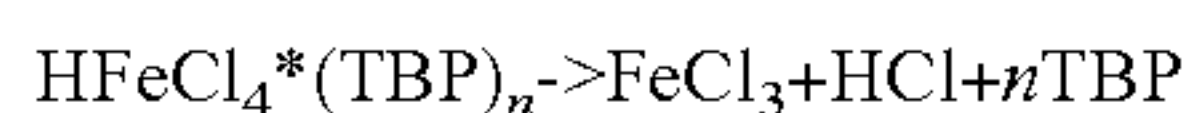


[0407] For example, solvent extraction of iron(III) from a chloride solution can be performed with tri-butyl phosphate (TBP) in kerosene as iron in this liquid environment is present in the form of a chloride complex ($FeCl_4^-$):



[0408] The extraction can be highly dependent on the chloride ion concentration. In fact, the higher chloride ion concentration, the stronger tendency for iron(III) complex formation and the better extraction. Iron(II) also forms similar chloride complexes ($FeCl_4^{2-}$), however, the $FeCl_4^{2-}$ -organic complex is less inclined for extraction at prevailing conditions.

[0409] To re-extract (strip) iron from the organic solvent, the organic solvent can be washed with pure water (for example nano water purity). Iron(III) can then be transferred to the water (strip solution) according to the expression:



[0410] Iron can be stripped as iron chloride. An equivalent amount of hydrochloric acid can also be washed out. The chloride concentration increases and the stripping of iron stops. Thus, the concentration of iron in the strip solution is limited by the simultaneous transfer of chloride ions.

[0411] The below presented examples are non-limitative and are used to better exemplify the processes of the present disclosure.

Example 1

Preparation of an Aluminum-Containing Material Sample

[0412] The aluminum-containing material (for example argillite) can be finely crushed in order to help along during the following steps. For example, micronization can shorten the reaction time by few hours (about 2 to 3 hours). In order to remove most of the iron, a leaching step at room temperature is optionally carried out between the crushing step and the calcination step. This operation is, for example, carried out with hydrochloric acid HCl (32 wt %) and an argillite/acid ratio (weight/volume) of 1:5 is used. Depending on experimental conditions (sizes of the particles, time of treatment, agitation system), about 65% to about 93% of the iron can then be dissolved. However, this leaching step can also bring in a certain percentage of the aluminum (0-5%). The last step of the preparation of argillite comprises calcining the pre-treated argillite. This can be accomplished at a calcinating temperature greater than 550° C. for a period of about 1 to 2 hours. For example, a heat treatment makes it possible to increase the quantity of extracted aluminum by about 30% to about 40% for the same period of time. In others words, the quantity of extracted aluminum is doubled. When leaching at

room temperature is carried out, a phase separation before calcination can be made in order to recover the acid and reduce heating costs.

Acid Leaching

[0413] Acid leaching can comprise reacting the crushed and roasted argillite with at least one acid solution (for example HCl) at elevated temperature during a given period of time. For example, the argillite/acid ratio can be of about 1:10 (weight/volume), the HCl concentration can be of about 6 M or about 18 to 20 wt %, the temperature can be of about 100° C. to about 110° C., and the reaction time can be of about 30 minutes to about 7 hours. Under such conditions, more than about 90% of the aluminum and about 100% of the iron can be extracted in addition to impurities. Alternatively, the leaching can be carried out at a temperature of about 150° C. to about 175° C. at a pressure of about 350 KPag to about 500 KPag during about 4 to about 7 hours.

[0414] During the second half of such a treatment (for example the last 2 or 3 hours), a portion of the excess acid can be recovered by flashing and condensation. Once the extraction is terminated, the solid (argillite impoverished in metals) can be separated from the liquid by decantation or by filtration, after which it is washed. The residual leachate and the washing water may be completely evaporated. The corresponding residue can thereafter be counter currently washed many times with water so as to decrease acidity and to lower the quantities of base used (for example, NaOH, KOH, $Ca(OH)_2$, $Mg(OH)_2$, etc.) that are required to adjust the pH during iron removal. The acid recovered can be re-utilized after having adjusted its titer either by adding either gaseous HCl, or by adding concentrated HCl (12 M). After the reaction, the titer of the acid can vary from about 4 M to about 6 M depending on experimental conditions. With respect to the solid, it represents about 65% to about 75% of the initial mass of argillite, it can be valorized and be used again either as an ion exchange resin, or as an adsorbent.

[0415] Alternatively, the HCl leaching can be carried out under pressure (so to increase the reaction temperature) into an autoclave.

[0416] The rare earth element(s) recovery can be made, for example, at this stage, after carrying out the above mentioned acid leaching.

[0417] For example, leaching at ratio 3.1/1.0 with 23 wt % HCl at 180° C. provided 96% extraction rate in terms of metal chlorides.

Removal of Iron

[0418] Several alternatives are proposed in the present disclosure for carrying out iron removal. For example, iron removal can be carried out by substantially selectively precipitating iron ions at certain pH values. Alternatively, some extracting agents can be used as described in WO2008141423. A membrane can also be used in combination with such extracting agents

[0419] For example, removal of iron can be carried out by ionic precipitation of the latter in basic medium for example at a pH of at least 10 or at a pH of about 11.5 to about 12.5. The pH can also be about 3 to about 6, or about 3 to about 5 or about 3 to about 4. Such a step can be made by adding a solution of NaOH, for example at a concentration of 10 M. Other bases such as KOH can also be used. Then, all that is required is to separate the solid portion from the liquid portion

by filtration, decantation or centrifugation and to rinse the solid by means of a diluted base, such as a solution of NaOH (for example NaOH at a concentration of 0.01 M to 0.02 M). Then, the solid is washed counter currently with water. The liquid portion comprises aluminum and alkaline-earths. A substantially complete removal of the iron and of nearly all the impurities (other metals) can thus be achieved as insoluble and washed hydroxides. Optionally, it is possible to recover iron by using a refining step by liquid-liquid extraction through a hollow fiber membrane.

[0420] Alternatively, removal of iron can be carried out by using an extracting agent and a hollow fiber membrane. Various extracting agents that could substantially selectively complex iron ions over aluminum ions (or aluminum ions over iron ions) could be used in such a step depending on an Al/Fe ratio. For example, extraction can be carried out by using HDEHP (or DEHPA) di(2-ethylhexyl)phosphoric acid) as an extracting agent adapted to complex iron ions. A concentration of about 1 M of HDEHP can be used in an organic solvent, such as heptane or any hydrocarbon solvent. Such an extraction can require relatively short contact times (few minutes). For example, the pH of the order of 2 can be used and aqueous phase/organic phase ratio can be of about 1:1. It was observed that it is possible to extract from 86% to 98% iron under such conditions. It will be understood that in the present case, iron is trapped in the organic phase. To recover iron in an aqueous phase, a reverse extraction with hydrochloric acid (2 M or 6 M) and organic phase/acidic phase ratio of about 1:0.5 can then be carried out. In such a case, the resulting aqueous phase is rich in Fe^{3+} ions.

[0421] The rare earth element(s) recovery can be made, for example, at this stage, after carrying out the above mentioned iron recovery.

[0422] With solvent extraction using countercurrent techniques, hydrochloric acid stripping and then contacting with MgO solution, therefore precipitating the rare earth elements in the form of hydroxide and then converting the products into their corresponding oxide into a calcination device.

Aluminum Recovery

[0423] This step can also be carried in various ways. For example, aluminum ions can be precipitated under the form of $\text{Al}(\text{OH})_3$ (for example an hydrated form of $\text{Al}(\text{OH})_3$) at a pH of about 7 to about 9 or about 7.5 to about 8.5 or about 8. Alternatively, the aluminum ions can be reacted with an extracting agent as described in WO2008141423.

[0424] The solution obtained from the previous step using either the precipitation or the extraction technique is relatively clean and mainly contains aluminum for example about 90% to about 95% or even as high as about 90% to about 99.8% (without the alkaline-earths in the case of precipitation). Recovery of the latter can be carried out by liquid-liquid extraction for example by using a same hollow fiber membrane and an extracting agent that is adapted to complex at least substantially selectively aluminum over other metals or residues. For example, bis(2,4,4-trimethylpentyl) phosphinic acid (such as the one sold under the name Cyanex™ 272) can be used as an extracting agent specific to aluminum. For example, this extracting agent can be used at a concentration

of about 20% v/v in an organic solvent such as heptane. The ratios between the aqueous phase and the organic phase can be of about 1:1 to about 1:3. For example, the extraction temperatures can be of about 40° C. and the pH can be maintained at about 2.5 to about 3.5. It was observed that such a technique makes it possible to extract more than 70-90% of the aluminum. After the aluminum has been trapped in the organic phase, it can be recovered in the form of a concentrate of Al^{3+} ions by using a back extraction. For example, the reverse extraction can be carried out at a temperature of about 40° C. with hydrochloric acid (for example at a concentration of 6 M). Under this condition, more than 90% of aluminum can be recovered.

[0425] The rare earth element(s) recovery can be made, for example, at this stage, after carrying out the above mentioned aluminum recovery.

[0426] Then, Al^{3+} can be converted into aluminum hydroxide (for example an hydrated form of $\text{Al}(\text{OH})_3$ by addition of a base such as NaOH. Finally, $\text{Al}(\text{OH})_3$ can be converted into alumina (alumina Al_2O_3) by calcinating $\text{Al}(\text{OH})_3$ for example at a temperature of about 800° C. to 1200° C.

[0427] Al^{3+} can also be converted into $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ and upon calcination HCl can be recovered and Al_2O_3 be produced.

[0428] Further purification can be performed by recrystallization.

Rare Earth Elements Recovery

[0429] Rare earth elements recovery can then be made, for example, at this stage by using any of the technology previously mentioned in the present disclosure for doing so. For example, it can be carried out by using a technology as defined in any one of FIGS. 3, 3A, 4A, 4B, 4C, 4D, 5A, 5B, 5C, 5D, 5E, 5F, 5G, 5H and 26.

[0430] The processes shown in FIGS. 5E, 5F, 5G and 5H are similar to the processes shown in FIGS. 5A, 5B, 5C and 5D, with the exception that they can comprise an extra purification step by using an ion exchange column, an optional plasma purification step, an extra acid regeneration step, and an extra calcination step.

[0431] For example, the at least one rare earth element contained in the residual solutions obtained from the above-mentioned process. For example, the at least one rare earth element can be in low concentration for example at a concentration of less than about 50, about 25, 15, 10, 5, 4, 3, 2 or 1 ppm in the lixiviate or leachate or a solution obtained during the process. The rare earth elements can be concentrated in the latter stage of the process prior to extraction with solvent (s). It was demonstrated that through an internal concentration loop, concentration can be significantly increased (for example from 100 to 1000 times) thereby providing more effective conditions for substantially selectively precipitating, extracting and/or isolating at least one rare earth element.

Example 2

[0432] As a starting material a sample of clay (argillite) was obtained from the Grande Vallée area in Québec, Canada.

[0433] These results represent an average of 80 tests carried out from samples of about 900 kg each. These tests were carried out by using a process as shown in FIG. 1 and FIG. 2.

[0434] Crude clay in the freshly mined state after grinding and classification had the following composition:

Al_2O_3 : 15%-26%;

SiO_2 : 45%-50%;

Fe_2O_3 : 8%-9%;

MgO : 1%-2%;

[0435] Rare earth elements: 0.04%-0.07%;

LOI: 5%-10%.

[0436] This material was thereafter leached in a two-stage procedure at 140-170° C. with 18-32 weight % HCl. The HCl solution was used in a stoichiometric excess of 10-20% based on the stoichiometric quantity required for the removal of the acid leachable constituents of the clay. In the first leaching stage of the semi-continuous operation (step 2), the clay was contacted for 2.5 hours with required amount or certain proportion of the total amount of hydrochloric acid. After removal of the spent acid, the clay was contacted again with a minimum 18 weight % hydrochloric acid solution for about 1.5 hour at same temperature and pressure.

[0437] The leachate was filtered and the solid was washed with water and analyzed using conventional analysis techniques (see step 3 of FIG. 1). Purity of obtained silica was of 95.4% and it was free of any chlorides and of HCl.

[0438] In another example, the purity of the silica was 99.67% through an extra leaching step.

[0439] After the leaching and silica removal, the concentration of the various metal chlorides was:

AlCl_3 : 15-20%;

FeCl_3 : 4-6%;

FeCl_2 : 0.5-2.0%;

MgCl_2 : 0.5-2.0%;

REE-Cl: 0.1-2%

Free HCl: 5-50 g/l

[0440] Spent acid was then crystallized using about 90 to about 98% pure dry hydrochloric acid in gas phase in two stages with less than 25 ppm iron in the aluminum chloride hexahydrate formed. The concentration of HCl in solution (aqueous phase) was about 22 to about 32% allowing 95.3% of Al_2O_3 recovery. The recovered crystallized material (hydrate form of AlCl_3 having a minimum purity of 99.8%) was then calcined at 930° C. or 1250° C., thus obtaining the α form of the alumina (1250° C.). The δ form being obtained at 930° C.

[0441] Another example was carried out at low temperature (decomposition and calcination at about 350° C.) and the δ form of the alumina was less than 2%.

[0442] HCl concentration in gas phase exiting the calcination stage was having a concentration of about 21 to about 32% by weight and was used (recycled) for crystallization of the AlCl_3 and MgCl_2 . Excess of hydrochloric acid is absorbed at the required and targeted concentration for the leaching steps.

[0443] Iron chloride (about 90% to about 95% in ferric form) is then sent to a hydrothermal process in view of its

extraction as pure hematite (Fe_2O_3). This can be done by using the technology described in WO 2009/153321 of low temperature hydrolysis with full heat recovery from calcining, pyrohydrolysis and leaching stage.

[0444] Before step 10 (in both processes of FIGS. 1 and 2) it was demonstrated that about 90 to about 98% by weight of the elements (Al, Fe, Mg and rare earths elements such as (Sc, Ga, Y, Ce) found in the starting material were recovered. It can be estimated that the processes for recovering rare earth elements from an aluminum-containing material disclosed in the present disclosure can be efficient for recovering about 90% of the rare earth elements. Thus, with respect to the examples of processes provided in FIGS. 1 and 2, it can be estimated that the overall yield for recovering the at least one rare earth element from the aluminum-containing material would be about 80% to about 90%.

[0445] Rare earth elements can be extracted from the mother liquor of the hydrolyzer (where silica, aluminum, iron and a great portion of water have been removed) following pre-concentration from crystallization to the hydrolyzer. In the form of chlorides the rare earth elements (RECl) are considerably concentrated and ready to be extracted. Rare earth elements have demonstrated to concentrate by a factor 5 to 10 in average within the hydrolyzer itself on a single pass through it (without any concentration loop). The concentration factors obtained for certain elements within the hydrolyzer (single pass) were as follows:

[0446] Ce: >6

[0447] La: >9

[0448] Nd: >7

[0449] Y: >9

[0450] For example, it can be carried out by using a technology as defined in any one of FIGS. 3, 4A, 4B, 4C, 4D, 5A, 5B, 5C, 5D, 5E, 5F, 5G, 5H and 26.

[0451] The person skilled in the art would thus clearly understand that such a concentration could be considerably more increased when carrying out a concentration loop.

[0452] Remaining magnesium chloride is sparged with dry and highly concentrated hydrochloric acid and then calcinated to MgO while recovering acid at its azeotropic point.

[0453] Mixed oxides containing other non-hydrolyzable components were then undergoing a pyrohydrolysis reaction at 700-800° C. and recovered acid (15-20.2% wt.) was rerouted for example to the leaching system.

Overall Yields Obtained:

[0454] Al_2O_3 : 93.0-95.03% recovery;

Fe_2O_3 : 92.65-99.5% recovery;

Rare earth elements: 95% minimum recovery (mixture);

MgO : 92.64-98.00% recovery;

Material discarded: 0-5% maximum;

HCl global recovery: 99.75% minimum;

HCl strength as feed to leaching 15-32% (aqueous); 95% (gas)

Red mud production: none.

Example 3

[0455] A similar feed material (bauxite instead of clay) was processed as per in example 2 up to the leaching stage and revealed to be easily leachable under the conditions established in example 2. It provided an extraction percentage of 100% for the iron and over 95% for aluminum. The process was found to be economically viable and no harmful by-products (red mud) were generated. A rare earth elements recovery (as a mixture) of about 90 to about 95% or about

91% (by weight as compared to the starting material) was observed. Samples tested had various concentrations of Al_2O_3 (up to 51%), Fe_2O_3 (up to 27%) and MgO (up to 1.5%). Gallium extraction of 97.0% was observed. Scandium extraction was 95%.

Example 4

[0456] Some test have been made so as to validate the processes described in FIGS. 4A, 4B, 5A, 5B, 5C and 5D.

[0457] Gallium chloride and rare earth chloride hydrates from Alfa Aesar GmbH & Co KG, Karlsruhe, Germany were used in the experiments. The products are of chemically pure quality (99.9%). Chemicals were dissolved in tap water to obtain a stock solution. Aluminum chloride and iron chloride are of technical grade.

Gallium and Rare Earth Elements Precipitation Tests

[0458] The different gallium and rare earth precipitation tests were carried out using limestone, magnesium oxide and/or caustic soda. As precipitation reagent, oxalic acid was used. The pH adjustment during the oxalate precipitation was carried out with ammonia (25%). At the end of the experiments, the precipitate was separated from the aqueous solution by filtration. The equilibrium solubility of rare earth hydroxides and rare earth oxalates in chloride media was measured at 25° C.

[0459] Hydroxide precipitation of gallium and scandium with limestone was carried out from a rare earth solution, containing 15 g/L Al, 180 g/L Fe(II), 220 mg/L Ga, 1.4 g/L Ce, 170 mg/L Y and 70 mg/L Sc. The aqueous solution was neutralized at elevated temperature to precipitate and remove gallium and rare earth elements. FIG. 6 shows the gallium and scandium hydroxide precipitation yield obtained as a function of pH value in aqueous solution (35 g/L HCl, Eh +380 mV).

[0460] The plotted curves in FIG. 6 show the dependency of gallium and rare earth precipitation yields as a function of the pH. An increase in the pH increases the gallium and scandium precipitation yield and approaches 98% for gallium and scandium at a pH around 2.0. FIG. 6 also shows that there is an increase in aluminum co-precipitation at pH levels higher than 2.0. No cerium and yttrium precipitate under these conditions. Therefore, it was shown that if the pH in the precipitation process is maintained at or below 2.0, gallium and scandium precipitates with minimizing aluminum, iron(II) and rare earth elements co-precipitation.

[0461] To investigate the influence on the iron(II) concentration on the gallium and scandium precipitation, iron(II) chloride in the order of 100 g/L Fe was added to the gallium and scandium feed solution. The following test parameters were defined:

Temperature: 25° C.

[0462] Stirrer speed: 400 rpm

Time: 1 h

[0463] Precipitation reagent: limestone

Final pH: 5.3

[0464] FIG. 7 shows, for the precipitation of gallium—the influence of iron(II) (aqueous solution (270 mg/L Ga, 90 mg/L Sc and 35 g/L HCl, Eh +380 mV). FIG. 7 above shows that the iron(II) concentration did not have significant effect on the precipitation of gallium.

[0465] The curves plotted in FIG. 8 show the influence of iron(II) contamination of scandium precipitation as a function of pH (aqueous solution (270 mg/L Ga, 90 mg/L Sc and 35 g/L HCl, Eh +380 mV). The conditions are the same than in FIG. 7. The precipitation pH of scandium increased from about pH 2 to about pH 3.5 which may have been due to the absence of iron in the aqueous feed solution. The final concentration of scandium at pH around 4 achieved 18 mg/L Sc, equivalent to a precipitation yield of 80%.

[0466] The gallium and scandium rich precipitates were washed with water and then dried at 105° C. and analysed to determinate co-precipitated rare earth elements. Table 1 shows the coprecipitation for aluminium, iron(II), cerium and yttrium and their concentrations in the resulting gallium and scandium precipitates achieved during the laboratory leaching test work.

TABLE 1

Co-precipitation for iron(II), cerium and yttrium from gallium and scandium hydroxide		
Leaching Parameter	Items	Value
Aluminium concentration in precipitate	g/kg	4-6
Iron(II) concentration in precipitate	g/kg	20-30
Losses of cerium	%	<0.5
Cerium concentration in precipitate	g/kg	1-2
Losses of yttrium	%	<0.5
Yttrium concentration in precipitate	g/kg	0.1-0.2

[0467] The results of gallium and scandium removal tests are summarised in table 2.

TABLE 2

Summary of gallium and scandium removal tests		
Gallium and Scandium Removal Parameter	Items	Value
Temperature	° C.	25 to 35
Time	min	15 to 30
Precipitation reagent	—	limestone
Initial pH value	—	0
Final pH value	—	2-3
Gallium precipitated	%	99.9
Scandium precipitated (containing Fe(II))	%	98
Scandium precipitated	%	80
Rare earth losses in solids	%	<1
Final Ga in filtrate	mg/l	<1
Final Sc in filtrate	mg/l	<2
Final Sc in filtrate (containing Fe(II))	mg/l	<20

Hydroxide Precipitation of Rare Earth Elements

[0468] Hydroxide precipitation of rare the earth elements with magnesium oxide and caustic soda carried out with a solution, containing 1.8 g/L Ce, 2.3 g/L Y, 1.8 g/L Er, 2 g/L Nd and 0.5 g/L Pr. The aqueous solution was neutralized with caustic soda at room temperature and with magnesium oxide at 65° C. to precipitate and remove the rare earth elements. To investigate the influence of pH on the rare earth hydroxide precipitation, the following test parameters were defined:

[0469] Temperature: 25° C. and 60° C.

[0470] Stirrer speed 400 rpm

[0471] Time: 1 h

[0472] Precipitation reagent: magnesium oxide and caustic soda

[0473] Final pH: 10

[0474] FIG. 9 shows that the precipitation of the rare earth hydroxides starts at pH 6 and have their maximum at pH around 8.0. In FIG. 9, an aqueous solution in which the initial pH was 1 and the Eh was +340 mV.

Oxalate Precipitation

[0475] A pre-neutralized aqueous solution from the hydroxide precipitation tests, containing 1.8 g/L Ce, 2.3 g/L Y, 1.8 g/L Er, 2 g/L Nd and 0.5 g/L Pr was heated up to 50 to 60° C. Oxalic acid slurry was added. The pH value was then adjusted by adding drop wise ammonia solution to precipitate and remove the rare earth elements. To investigate the influence on the amount of precipitation reagent, the following test parameters were defined:

[0476] Temperature: 60° C.

[0477] Stirrer speed: 400 rpm

[0478] Time: 1 h

[0479] Precipitation reagent: oxalic acid as di-hydrate

[0480] Final pH: 1.2

[0481] FIG. 10 below shows the solubility of the rare earth oxalates with increasing oxalic acid concentration at constant acidity (pH 1.2). The precipitation concentration ranged from 0.06 mol/L to 1 mol/L oxalic acid. (aqueous solution (LRE and HRE, final pH 1.2, Eh +340 mV).

[0482] For the given acidity, the solubility of the rare earth oxalates decreases as oxalic acid concentration increase and reached a precipitation yield of more than 99% all of the investigated rare earth elements if the added oxalic acid concentration is 0.15 mol/L or more.

[0483] To investigate the influence of iron(II) concentration on the precipitation of the rare earth elements, the following test parameters were defined:

[0484] Temperature: 60° C.

[0485] Stirrer speed: 400 rpm

[0486] Time: 1 h

[0487] Precipitation reagent: oxalic acid

[0488] Iron(II) concentration: 100

[0489] Final pH: 1.2

[0490] The curve plotted in FIG. 11 shows the rare earth elements and iron precipitation as a function of oxalic acid concentration at constant acidity (pH 1.2). The figure indicates that precipitation of the rare earth elements do not proceed at high iron(II) contamination.

The results of the rare earth elements removal tests are summarised in table 3.

TABLE 3

Summary of rare earth elements precipitation tests		
REE Precipitation Parameter	Items	Value
Temperature	° C.	60
Time	min	60
Precipitation reagent	—	limestone
Initial pH value	—	3
Final pH value	—	8
Yttrium precipitated (as HRE)	%	>99
Cerium precipitated (as LRE)	%	>99
Final Y in filtrate	mg/l	<5
Final Ce in filtrate	mg/l	<5

Solvent Extraction Tests

[0491] To simulate a counter current solvent extraction operation, metal equilibrium tests were performed. All

experiments are carried out at 25° C. All investigations are carried out in bench-scale laboratory equipment.

[0492] The organic solutions were contacted for about 10 to 15 minutes in shaking funnels or in stirred beakers under fairly high speed mixing at different organic to aqueous (O/A) ratios.

[0493] The pH adjustment during the solvent extraction is carried out using caustic soda solution (10%). After phase separation, the resulting aqueous and organic phases were saved and analysed.

Gallium and Scandium Solvent Extraction Results

[0494] Based on the selectivity for gallium and scandium over yttrium, other trivalent rare earth, and aluminium, the reagent tri-butyl phosphate (TBP) was chosen. On the other hand, iron(III) was being co-extracted with TBP. Thus, before recovering gallium and scandium, iron(III) was removed either by solvent extraction or pre-treated by metallic iron in order to remove of iron(III) by the reduction. FIG. 12 shows equilibrium data for extraction of iron from a iron(III) chloride solution. The organic solution contained 90 vol.-% TBP in aromatic kerosene (Solvesso150).

[0495] Co-extraction of gallium by tri-butyl phosphate from iron(III) chloride solution is indicated in table 4.

TABLE 4

Gallium co-extraction						
Org. solution (90 vol.-% TBP in kerosene)						
Aqueous solution (40% FeCl ₃ , 270 mg/l Ga, Eh 500 mV)						
Organic ml	Aqueous ml	Aq/Org —	Org.-Ga mg/l	Aq.-Ga mg/l	$D_{Ga} = \frac{C_{Ga}}{C_{Ga}}$	$P_{Ga} \%$
101.5	8.5	0.08	6.9	188	0.037	30.4
71.5	8.5	0.12	9.5	190	0.050	29.6
51.3	8.7	0.17	12.4	197	0.063	27.0
41	19	0.46	43.6	176	0.248	34.8
43	38	0.86	124	130	0.952	51.9
20	60	3.00	453	119	3.807	55.9

[0496] Co-extracted gallium can be partially removed by scrubbing with water at high phase ratio. This scrubbing reduces the gallium losses from the loaded organic solution. Equilibrium data for scrubbing of gallium from the loaded organic solution is shown in FIG. 13 (equilibrium curve. org. solution (90 vol.-% TBP, containing 110 g/L Fe, 0.13 g/L Ga) aqueous solution (water).

[0497] The equilibrium data for stripping of iron from the loaded organic solution is shown in FIG. 14 (org. solution (90 vol.-% TBP, containing 110 g/L Fe, 0.13 g/L Ga) Aqueous solution (water).

[0498] The gallium and scandium feed solution was prepared by dissolution of the gallium/scandium precipitate from a hydrochloric acid solution, containing 10 mol/L HCl. The experiments were carried out with 50 vol.-% TBP diluted in aliphatic kerosene (D85). Isodecanol was used in the experiments as modifier to prevent third phase formation. Equilibrium data for gallium and scandium extraction is shown in FIG. 15 (org. solution (50 vol.-% TBP in kerosene; aq. solution 6 g/L Ga, 2.2 g/L Sc and 10 mol/L HCl).

[0499] FIG. 16 shows the co-extraction of hydrochloric acid during the gallium and scandium extraction (org. solution (50 vol.-% TBP in kerosene; aq. solution (6 g/L Ga, 2.2 g/L Sc and 10 mol/L HCl). The organic solvent is then further

loaded with gallium and scandium for conducting scandium scrubbing and gallium stripping experiments.

[0500] To remove scandium from the loaded organic solution, 5 mol/L, 6 mol/L and 7 mol/L HCl solutions at O/A ratio of 1 to 1 were used. This scrubbing significantly reduces the quantity of scandium from the loaded organic solution. The influence on the hydrochloric acid scrub solution of scandium scrubbing efficiency is shown in table 5.

TABLE 5

Scandium scrubbing tests					
Org. solution (50 vol.-% TBP, containing 1.3 g/l Ga, 1.2 g/l Sc, initial Ga/Sc ratio 1.07).					
Aq. solution (Hydrochloric acid solution)					
Scrub sol mol/l HCl	Aq/Org —	D_{Ga} C_o/C_a	D_{Sc} C_o/C_a	S D_{Ga}/D_{Sc}	Ga/Sc ratio $[C_{Ga}/C_{Sc}]_{org}$
5	1.0	266	0.034	7704	31.9
6	1.0	710	1.553	514	1.75
7	1.0	799	5.667	125	1.25

[0501] Equilibrium data for scandium scrubbing from the loaded organic solution is shown in FIG. 17. (org. solution (50 vol.-% TBP, 7.3 g/L Ga, 1.6 g/L Sc); aqueous solution (Water)).

[0502] Equilibrium data for gallium stripping from the loaded organic solution is shown in FIG. 18 (org. solution (7.5% TBP in kerosene, 0.4 g/L Ga; aqueous solution (water)).

[0503] The composition of aqueous feed and raffinate during the solvent extraction tests are summarised in Table 6.

TABLE 6

Composition of the aqueous feed and raffinate Org. solution (50 vol.-% TBP in kerosene)Aq. solution (6 g/L Ga, 2.2 g/L Sc and 10 mol/L HCl)			
Metal	Aqueous feed g/l	Raffinate mg/l	Extraction Efficiency %
Gallium	66	<5	99
Scandium	2.2	<5	99

[0504] First, scrubbing of scandium and co-extracted hydrochloric with water at very high O/A ratio resulted in a scandium chloride solution. Scrubbing is selective for scandium and leaving gallium in the scrubbed organic solution. Gallium was then stripped from the resulting scrubbed organic solution by water at O/A ratio of 2 to 1.

Extraction of Light and Heavy Rare Earth Elements

[0505] As previously shown, the extraction of rare earth elements can be depending on the hydrogen ion (H⁺) concentration. Consequently organo-phosphorus extractants are pH dependent extractants. Commercial reagents available such as di(ethylhexyl)phosphoric acid (D2EHPA), di(ethylhexyl)phosphonic acid (Ionquest 801) can be used. The selectivity is calculated as the quotient of the distribution factors of yttrium to that of cerium. As shown in FIG. 19 (org. solution (10 vol.-% reagent in kerosene; aq. solution (6.4 g/L Y, 107 g/L Ce, initial pH 1.5, Eh +430 mV. below, the yttrium/cerium selectivity for Ionquest 801 is raising until pH 1 and then falling.

[0506] Based on the selectivity for yttrium over cerium, di(ethylhexyl)phosphonic acid (Ionquest 801) was chosen. The experiments were carried out with 10 vol.-% Ionquest

801 diluted in aliphatic kerosene (D85). No modifier was used in the experiments. Yttrium and cerium extraction dependency of pH in chloride media is shown in FIG. 20 (extraction of cerium and yttrium in chloride solution with di(ethylhexyl)phosphonic acid (Ionquest 801) and di(ethylhexyl)phosphoric acid (D2EHPA).)

Extraction of Yttrium

[0507] The reagent di(ethylhexyl)phosphonic acid (Ionquest 801) was chosen. The experiments were carried out with 10 vol.-% Ionquest 801 diluted in aliphatic kerosene (D85). No modifier was used in the experiments. The pH value during the yttrium extraction was kept constant at pH 1.4 by adjusted drop wise with sodium hydroxide solution (2 mol/L NaOH). Equilibrium data for yttrium extraction from an aqueous solution containing yttrium and cerium is shown in FIG. 21 (org. solution (10 vol.-% Ionquest 801 in kerosene; aq. solution (6.4 g/L Y, 107 g/L Ce, initial pH 1.5, Eh +430 mV)).

[0508] The yttrium recovery rate was more than 99%. The maximum yttrium loading of 10% vol.-% Ionquest 801 reagent was about 10 g/L yttrium.

[0509] Smaller quantities of co-extracted cerium were removed by scrubbing with diluted hydrochloric acid. This measure significantly reduces the quantity of cerium from the loaded organic. Equilibrium data for cerium scrubbing from the loaded organic solution is shown in FIG. 22 (org. solution (10 vol.-% Ionquest 801, containing 0.1 g/l Ce; aq. solution 1 mol/l HCl)).

[0510] Measured concentrations in aqueous feed and raffinate in the yttrium extraction experiments are shown in table 7.

TABLE 7

Composition of the aqueous feed and raffinate Org. solution (10 vol.-% Ionquest 801 in kerosene) Feed solution (6.4 g/l Y, 107 g/l Ce, initial pH 1.5, Eh +430 mV)			
Metal	Aqueous feed g/l	Raffinate g/l	Extraction Efficiency %
Yttrium	6.4	0.1	98
Cerium	107	107	0.2

[0511] Equilibrium data for yttrium stripping from loaded organic solution is shown in FIG. 23 (org. solution (10 vol.-% Ionquest 801 in kerosene, containing 1 g/L Y); aqueous solution (3.5 mol/L HCl)).

Separation of Dysprosium and Erbium

[0512] The feed solution was prepared by dissolution of dysprosium chloride, erbium chloride and yttrium chloride in tap water. The experiments were carried out with tri-butyl phosphate (TBP), Alamine® 336 and Aliquat® 336 diluted in aliphatic kerosene (D85). The pH value was adjusted at pH 3 by drop wise addition of ammonia solution (25%). The organic solutions were contacted for about 10 to 15 minutes in stirred beakers. The organic to aqueous (O/A) ratio was 1/1. The separation and purification of dysprosium and erbium by TBP, Alamine® 336 and Aliquat® is shown in Table 8.

TABLE 8

Dysprosium and erbium separation tests Org. solution of TBP, Alamine ® 336 and Aliquat ® 336 Aq. solution (6.7 g/l Dy, 7.1 g/l Er, 6.2 g/l Y, initial pH 3 in 1 mol/ l NH ₄ SCN)		
Extractant	S (D _{Dy} /D _Y)	S (D _{Er} /D _Y)
TBP	7.2	5.7
Alamine ® 336	0.6	0.8
Aliquat ® 336	1.1	2.3

[0513] Based on the selectivity for dysprosium and erbium over yttrium, the reagent tri-butylphosphate (TBP) was chosen. The experiments were carried out with 80 vol.-% TBP diluted in aliphatic kerosene (D85). No modifier was used in the experiments. The influence of ammonium thiocyanate concentration on the extraction and separation of dysprosium and erbium from yttrium was tested. Equilibrium data for dysprosium and erbium extraction are shown in table 9.

TABLE 9

Dysprosium and erbium separation tests Org. solution (80 vol.-% TBP in kerosene) Aq. solution (6.7 g/l Dy, 7.1 g/l Er, 6.2 g/l Y, initial pH 3 in 1 mol/ l NH ₄ SCN)		
NH ₄ SCN mol/l	S (D _{Dy} /D _Y)	S D _{Er} /D _Y)
0	7.9	24
0.3	2.9	2.3
0.5	2.6	2.4
0.75	2.5	2.4
1.0	2.5	2.3

[0514] Co-extracted yttrium is removed by scrubbing with water at high O/A ratio. This scrubbing significantly reduces the yttrium losses from the TBP loaded organic solution. Equilibrium data for yttrium scrubbing from the loaded organic solution is shown in FIG. 24 (org. solution (80 vol.-% TBP in kerosene, 1.2 g/L Y); aqueous solution (Water).
[0515] Finally, equilibrium data for dysprosium stripping with water are shown in FIG. 25 (org. solution (80 vol.-% TBP in kerosene, 8.4 g/l Dy); aqueous solution (water).

Summary of the Solvent Extraction Tests

[0516] The tests have resulted in the following examples of extraction conditions, applicable for the iron(III) aqueous feed solution (Table 10).

TABLE 10

Selected conditions for iron(III) removal		
Iron Removal	Selected conditions	
TBP concentration	%	90
Modifier (Isodecanol) concentration	%	—
Aromatic kerosene (Solvesso 150)	%	10
Surface loading, aqueous continuous (35° C.)	m/h	2-3
Iron loading	g/l	100
Iron extraction yield	%	90
Iron raffinate concentration	g/l	20
Gallium co-loading	mg/l	100-130

[0517] The tests have resulted in the following examples of extraction conditions, applicable for the gallium and scandium aqueous solution (Table 11).

TABLE 11

Selected conditions for extraction of gallium and scandium.		
Gallium and Scandium Recovery	Selected conditions	
TBP concentration	%	50
Modifier (Isodecanol) concentration	%	15-20
Aliphatic kerosene	%	30-35
Surface loading, aqueous continuous (25° C.)	m/h	2-3
Gallium loading	g/l	30-35
Gallium extraction yield	%	>99
Gallium raffinate concentration	mg/l	<1
Scandium loading	g/l	10-15
Scandium extraction yield	%	99
Scandium raffinate concentration	mg/l	10-20

[0518] Gallium was calcined and the purity of the obtained Ga₂O₃ was 99.99+%. The impurities were Cl at 8.9 ppm and Al at 1.1 ppm.
[0519] Scandium was also calcined and the obtained purity of Sc₂O₃ was greater than 99.9%. The main impurities were S at 260 ppm and Zr at 390 ppm
[0520] The tests have resulted in the following examples of extraction conditions, applicable for the rare earth aqueous solution (Table 12).

TABLE 12

Selected conditions for extraction of rare earth (yttrium)		
Yttrium Recovery	Selected conditions	
lonquest 801 concentration	%	10
Aliphatic kerosene(D85)	%	90
Surface loading, aqueous continuous (25° C.)	m/h	2-3
Yttrium loading	g/l	10
Yttrium extraction yield	%	>98
Yttrium raffinate concentration	mg/l	10-20

[0521] The tests have resulted in the following proposed extraction conditions, applicable for the separation of heavy rare earth from yttrium strip liquor (Table 13).

TABLE 13

Selected conditions for extraction of heavy rare earth (Dy, Er)		
HRE (Dy, Er) Removal	Selected conditions	
TBP concentration	%	80
Aliphatic kerosene(D85)	%	20
Surface loading aqueous continuous (25° C.)	m/h	3-4
HRE loading	g/l	10
HRE extraction yield	%	99
HRE raffinate concentration	mg/l	5-10

[0522] The recovery procedure of gallium, yttrium and scandium preceded by iron(III) removal, followed by neutralization and precipitation of gallium and scandium has been demonstrated. To prevent and/or reduce iron coprecipitation, remaining iron(III) can be removed by further treatment (reduced) by using iron metal.
[0523] The following six main process sections were investigated:
Section 1: Iron(III) Removal. Removal of iron(III) from feed solution by solvent extraction using tri-butyl phosphate (TBP) in kerosene;

Section 2: Final Iron Removal. Removal of iron by reduction using metallic iron;

Section 3: Gallium and Scandium Precipitation. Removal of gallium and scandium using limestone or magnesium oxide;

Section 4: Gallium and Scandium Separation. Separation and recovery of gallium and scandium from re-leach solution containing 10 moth hydrochloric acid and based on solvent extraction using the tri-butyl phosphate (TBP) in kerosene;

Section 5: Yttrium and other rare earth precipitation. Removal of yttrium and other rare earth elements by neutralization and precipitation using limestone, followed by re-leaching in diluted hydrochloric acid;

Section 6: Yttrium Recovery. Separation and recovery of yttrium from the resulting solution in section 5 by solvent extraction using di(ethylhexyl) phosphonic acid (Ionquest 801); and

Section 7: Yttrium Separation from HRE. Separation and recovery of yttrium from heavy rare earth, mainly dysprosium and erbium by solvent extraction using tri-butyl phosphate (TBP) in kerosene.

Iron(III) Removal

Iron(III) Solvent Extraction

[0524] The prepared aqueous feed solution, containing 40% iron(III) chloride and 270 mg/L of gallium (201) was fed to the iron removal circuit. Iron was counter-currently extracted with an organic solution containing 90% TBP dissolved in aromatic kerosene (Solvesso150) (202). The achieved iron extraction yield was 90%. Co-extracted gallium was accumulated in the organic phase to 0.13 g/L gallium. The resulting organic solution (203), containing iron and small amounts of gallium, was fed to the scrubbing circuit. Here, gallium was counter-currently scrubbed with an aqueous water solution (204) at high phase ratio. The organic solvent was then sent to a stripping circuit. Here, iron (206) is counter-currently stripped with water (207) before the organic solution (205) was returned back to the extraction circuit.

Iron(III) Reduction

[0525] Co-extraction of iron(III) can be prevented and/or by prior reduction to iron(II) using iron (0). The resulting raffinate (209), containing aluminum, gallium, scandium, rare earth elements and extracted iron(III) was treated with stoichiometric amounts of iron powder (210) to eliminate the iron(III) ions. Starch can also be used for carrying out the reduction.

Gallium and Scandium Recovery

Gallium and Scandium Precipitation

[0526] The precipitation and recovery of gallium and scandium was introduced to separate gallium and scandium from other rare earth elements and to pre-concentrate both gallium and scandium for further treatment. Depleted from iron(III), the resulting filtrate (211) was then fed to a primary gallium and scandium removal step. Here limestone (212) was added as neutralization reagent. In this step, the solution was maintained at constant pH during 15 to 30 min and under controlled RedOx conditions at low pH level. A precipitation yield of 99% of the gallium and scandium was achieved. The rare earth elements were detected with very low concentra-

tion in the gallium and scandium precipitate. The filter product (225) was fed to a dewatering system. The resulting slurry (213) was then prepared for re-leaching in concentrated hydrochloric acid solution (214).

Gallium and Scandium Solvent Extraction

[0527] The resulting filtrate (215) from the gallium and scandium re-leaching step was fed to the gallium and scandium separation circuit. Gallium and scandium are counter-currently extracted with an organic solution containing 50 vol.-% TBP dissolved in aliphatic kerosene (D85) (216). The achieved gallium and scandium extraction yield was more than 99%.

[0528] Co-extracted iron was accumulated in the organic phase to 0.2 g/L Fe. The resulting organic solution (218), containing gallium and scandium and small amounts of iron was fed to the scrubbing circuit. Here, scandium was counter-currently scrubbed with an aqueous water (219) solution at high phase ratio so as to provide product (221). The organic solvent (220) was then sent to a stripping unit where gallium was counter-currently stripped with water (222) before the organic solution (223) is returned back to the extraction circuit and gallium (224) is recovered. A raffinate of hydrochloric acid is also recovered (217).

[0529] Yttrium Recovery

Rare Earth Hydroxide Precipitation

[0530] The filtrate (225) from the gallium and scandium precipitation step was fed to a further neutralization circuit. Here, rare earth elements are precipitated with limestone (226) by raising the pH to 8 during 60 min under controlled RedOx potential and at elevated (60° C.) temperature. A precipitation of more than 99% of the investigated rare earth elements was achieved. Remaining iron(II) will precipitate together with the rare earth elements. The precipitate (227) was then prepared for re-leaching in concentrated hydrochloric acid solution (228).

Primary Yttrium Solvent Extraction

[0531] The resulting product (229) from the gallium and scandium precipitation step will be fed to the extraction circuit for yttrium. Yttrium is counter-currently extracted with an organic solution (230) containing 10 vol.-% Ionquest 801 dissolved in aliphatic kerosene (D85). The achieved yttrium extraction yield was more than 99%. Co-extracted cerium was accumulated in the organic phase to 0.1 g/L Ce.

[0532] Due to the high cerium concentration in the aqueous solution, cerium could be transferred to the strip liquor by aqueous entrainment of leach solution. Therefore an extra single scrubbing step can be included to avoid cerium contamination. For example, the organic phase (232) can be treated with a scrub solution (233) such as 1 N HCl so as to remove cerium and obtain composition (234). The raffinate of LRE (Ce, Nd, Eu, Pr) (231) can eventually be treated so as to separate them from one another and optionally purify them (see FIG. 5G).

[0533] The resulting organic solution (235), containing yttrium is fed to the stripping circuit. Here, yttrium is counter-currently stripped with a solution, containing 3.5 mol/L hydrochloric acid (236). Finally, before returning the organic solution back to the primary yttrium extraction, part of the

organic reagent has to be washed with diluted caustic soda solution in one mixersettler stage for organic regeneration and scandium removal.

Final Yttrium Solvent Extraction

[0534] In the second solvent extraction process, dysprosium and erbium are removed from the yttrium strip liquor (237) after neutralization. Dysprosium and erbium are counter-currently extracted with an organic solution containing 80 vol.-% tri-butyl phosphate (TBP), dissolved in aliphatic kerosene (D85) (238), thereby yielding the raffinate of yttrium (239). A heavy rare earth extraction yield of more than 99% is achieved under controlled pH conditions. The resulting organic solution (240), containing heavy rare earth and small amounts of yttrium, is fed to the scrubbing function. Here, the yttrium (242) is scrubbed with water (241) at high phase ratio, counter-currently in multistage mixersettler equipment. The scrubbing liquor (242) is returned to the feed solution. The organic solvent, depleted from yttrium (243) is stripped with water (244) and returned to the extraction loop. The dysprosium and erbium strip liquor (245), is the feed solution for dysprosium and erbium separation.

[0535] The obtained yttrium was calcined into Y_2O_3 and a purity of 99.9+% was obtained. The impurities were Si at 26 ppm, Dy at 51 ppm and Al at 6.2 ppm.

Example 5

[0536] Other tests have been made by using a process as shown in FIG. 26. Leaching of the rare earth hydroxide filter cake (327) was carried out using hydrochloric acid (328). The person skilled in the art would recognize that the process shown in FIG. 26 can be used for treating various compositions including the precipitate (227) of FIG. 5c. For example, the precipitate (327) of FIG. 26 can be the same than the precipitate (227) from FIG. 5c.

[0537] The pregnant leach solution (329) (after fine filtration) was the feed solution to the rare earth separation steps. The present aqueous feed solution comprises cerium, praseodymium, neodymium, europium, dysprosium, erbium and yttrium is contacted with D2EHPA or Ionquest 801 in kerosene. Alkali is used to adjust the pH during the extraction procedure. Dysprosium, erbium and also yttrium (HRE) are extracted and leaving cerium, praseodymium, neodymium and europium (LRE) in the raffinate (331).

[0538] The loaded organic phase is then selectively scrubbed with hydrochloric acid (1 to 2 M HCl) to remove the co-extracted LRE. The extract, contained dysprosium, erbium and yttrium, is then stripped with hydrochloric acid (3 to 4 M HCl) (336).

[0539] The separation of yttrium from the strip liquor (337) can be done by extracting it with tri-butyl phosphate (TBP) in kerosene. The treatment can be done in a multi stage procedure, and ending up in a final stripping of the loaded organic with water (344). All HRE substantially selectively extracted, leaving yttrium in the raffinate (339). The strip liquor (345), containing HRE, forms the source for further separation of the heavy rare earth elements (HRE).

Separation of Erbium from Dysprosium

[0540] The final strip liquor from the yttrium separation process (345) containing dysprosium and erbium was treated by solvent extraction using D2EHPA or Ionquest 801 in kerosene, leaving dysprosium in the raffinate (347). Alkali is used to adjust the pH during the extraction circuit. The loaded

organic phase is then scrubbed with hydrochloric acid (2 to 3 M HCl) to remove the co-extracted dysprosium. The extract, containing erbium, is then stripped with hydrochloric acid (3 to 4 M HCl) (346) so as to yield the strip liquor of erbium (348).

[0541] The so-obtained dysprosium was calcined in order to produce Dy_2O_3 having a purity of 99.9+%. Other impurities were mainly Yb at 440 ppm and Ca at 100 ppm.

[0542] The so-obtained erbium was calcined in order to produce Er_2O_3 having a purity of 99.9+%. Other impurities were mainly Y at 390 ppm and Al at 140 ppm.

Separation of Cerium by Oxidation and Cerium Precipitation

[0543] The raffinate (331A) from the primary separation is fed to oxidation and cerium precipitation unit. The oxidation of cerium is achieved by addition of an oxidation reagent. For example, sodium hypochlorite (349) can be used. The precipitation of cerium hydroxide can be carried at a pH of about 0.5 to about 1.5 or pH of about 1 after adding of alkali (350). The outflow from the cerium oxidation (352) is fed to the europium separation circuit. The filter cake (351), containing cerium hydroxide was washed with acidic water, dewatered and stored for further processing.

[0544] The so-obtained cerium was calcined into Ce_2O_3 and a purity of 99.5+% was obtained. The impurities were K at 330 ppm, Pr at 280 ppm and Y at 50 ppm.

Separation of Europium

[0545] The resulting filtrate (352) from the cerium recovery step was used to separate europium from praseodymium and neodymium. The aqueous feed solution was contacted with D2EHPA or Ionquest 801 in kerosene. Europium was extracted and leaving praseodymium, neodymium in the raffinate (354). Alkali was used to adjust the pH during the extraction circuit. A scrubbing section removed co-extracted praseodymium and neodymium by using weak hydrochloric acid (0.5 to 1.5 M HCl). The extract, containing europium, was then stripped with hydrochloric acid (2 to 3 M HCl) (353).

Reduction and Precipitation of Europium

[0546] The reduction of europium(III) was achieved by addition of an reduction reagent. For example, europium (355) can be reduced by zinc powder or alternatives (361). The precipitation of europium sulphate can be carried out after addition of sodium sulphate (362). The outflow from the europium reduction circuit was fed to the effluent treatment. The filter cake (363), containing europium sulphate was washed with acidic water, dewatered and stored for further processing.

Separation of Neodymium from Praseodymium

[0547] The raffinate (354) from the europium separation consists mainly of praseodymium and neodymium. The separation of praseodymium and neodymium was carried out with D2EHPA or Ionquest 801 in kerosene. Neodymium was extracted, leaving praseodymium in the raffinate (357). Alkali was used to adjust the pH during the extraction circuit. The loaded organic phase was then scrubbed with hydrochloric acid (2 to 3 M HCl) (356) to remove the co-extracted praseodymium. The organic extract (358), presently containing neodymium, was then stripped with hydrochloric acid (3 to 4 M HCl) (359) so as to obtain the strip liquor of neodymium (360).

[0548] The so-obtained neodymium was calcined into Nd₂O₃ and a purity of 99.9+% was obtained. The impurities were K at 330 ppm, Pr at 280 ppm and Y at 50 ppm.

[0549] In order to demonstrate the versatility of the processes of the present disclosure, several other tests have been made so as to shown that these processes can be applied to various sources of starting material.

Example 6

[0550] Another starting material has been used for preparing acidic compositions comprising various components. In

fact, a material that is a concentrate of rare earth elements and rare metals (particularly rich in zirconium) has been tested. Table 14 shows the results of the leaching carried out on such a starting material using a similar process as shown in FIGS. 1 and 2 and as detailed in Examples 1-3. It can thus be inferred from the results shown in Table 14 that the rare earth elements and rare metals extracted and present in the obtained leaching composition can eventually be isolated by the processes of the present disclosure such as, for example, by those presented in Examples 4 and 5. The results obtained were superior by at least 20% as compared to leaching carried out with H₂SO₄.

TABLE 14

Tests made on a zirconium rich material.				
Raw material	Composition measure and/or evaluated (% wt.)	Average measured for testing (% wt.)	Extraction rate measured (ALP) (%)	O All Orbite process recovery (%)
Al ₂ O ₃	6.12	6.12	89.65	86.97
Fe ₂ O ₃	15.80	15.80	99.50	97.51
SiO ₂	36.00	36.00	0.000	99.997
MgO	3.08	3.08	99.75	92.66
Na ₂ O	1.13	1.13	99.50	99.50
K ₂ O	2.12	2.12	99.50	99.50
CaO	6.10	6.10	99.50	99.00
S total	0.22	0.22		100.00
F	1.98	1.98	99.50	99.00
TiO ₂	0.13	0.13	0.000	99.03
V ₂ O ₅	0.00	0.00	98.00	96.04
P ₂ O ₅	1.10	1.10	98.00	96.04
MnO	0.43	0.43	98.00	96.04
ZrO ₂	12.43	12.43	22.70	20.43
Cr ₂ O ₃	0.00	0.00	0.00	0.00
Ce ₂ O ₃	3.05	3.045	97.31	92.98
La ₂ O ₃	1.34	1.337	99.55	92.68
Nd ₂ O ₃	1.55	1.551	98.40	94.79
Pr ₂ O ₃	0.37	0.375	99.75	97.52
Sm ₂ O ₃	0.15	0.151	88.75	84.80
Dy ₂ O ₃	0.09	0.089	80.35	76.77
Er ₂ O ₃	0.03	0.030	72.60	69.37
Eu ₂ O ₃	0.03	0.027	85.57	81.76
Gd ₂ O ₃	0.21	0.205	82.85	79.16
Ho ₂ O ₃	0.01	0.013	77.10	73.67
Lu ₂ O ₃	0.00	0.003	60.15	57.47
Tb ₂ O ₃	0.02	0.022	78.05	74.58
Th	0.02	0.022	88.10	84.18
Tm ₂ O ₃	0.00	0.004	66.85	63.88
U	0.01	0.014	81.90	78.26
Y ₂ O ₃	0.30	0.300	72.70	69.46
Yb ₂ O ₃	0.02	0.023	62.80	60.01
Ga ₂ O ₃	0.02	0.016	96.90	92.59
Sc ₂ O ₃	0.00	0.003	95.00	90.77
LOI (inc. water)	6.122023973	6.12		

Example 7

[0551] Other tests have been made in a similar manner as described in Example 6. In the present example, carbonatite has been used as a starting material. (see table 15 below).

TABLE 15

Tests made on carbonatite				
Raw material	Composition measure and/or evaluated (% wt.)	Average measured for testing (% wt.)	Extraction rate measured (ALP) (%)	O All Orbite process recovery (%)
Al ₂ O ₃	0.70	0.70	84.31	81.61
Fe ₂ O ₃	11.22	11.22	94.14	92.15
SiO ₂	2.11	2.11	0.00003	99.997
MgO	6.50	6.500	100	96.25

TABLE 15-continued

Tests made on carbonatite				
Raw material	Composition measure and/or evaluated (% wt.)	Average measured for testing (% wt.)	Extraction rate measured (ALP) (%)	O All Orbite process recovery (%)
Na ₂ O	0.07	0.07	92.54	90.55
K ₂ O	0.18	0.181	37.33	37.33
CaO	16.51	16.51	100	98.00
TiO ₂	0.00	0.000	0.00000	100.000
V ₂ O ₅	0.00	0.000	0	100.000
P ₂ O ₅	0.00	0.000	0	100.000
MnO	0.00	0.000	0	100.000
ZrO ₂	0.00	0.000	0	100.000
Cr ₂ O ₃	0.00	0.000	0	100.000
Ce ₂ O ₃	1.19	1.195	64.04	61.190
La ₂ O ₃	0.46	0.463	63.86	61.018
Nd ₂ O ₃	0.45	0.448	81.46	77.835
Pr ₂ O ₃	0.14	0.142	67.59	64.582
Sm ₂ O ₃	0.03	0.033	65.32	62.413
Dy ₂ O ₃	0.00	0.000	78.12	74.644
Er ₂ O ₃	0.00	0.000	86.15	82.316
Eu ₂ O ₃	0.01	0.007	66.45	63.493
Gd ₂ O ₃	0.01	0.013	54.46	52.037
Ho ₂ O ₃	0.00	0.000	83.12	79.421
Lu ₂ O ₃	0.00	0.000	88.86	84.906
Tb ₂ O ₃	0.00	0.001	41.42	39.577
Th	0.06	0.065		
Tm ₂ O ₃	0.00	0.000	90.70	86.664
U	0.01	0.007		
Y ₂ O ₃	0.00	0.000	84.68	80.912
Yb ₂ O ₃	0.00	0.000	85.11	81.323
Ga ₂ O ₃	0.00	0.000	0	0.000
Sc ₂ O ₃	0.00	0.000	0	0.000
LOI (inc. water)		60.33		

Example 8

[0552] Another series of tests was performed on argillite using processes as per previous examples.

The initial composition measured was:

TABLE 16

Raw material initial composition	
Element	Composition measured (wt.)
Al ₂ O ₃	24.00%
Fe ₂ O ₃	8.51%
MgO	1.33%
Na ₂ O	1.06%
K ₂ O	2.86%
Ce ₂ O ₃	176 ppm
La ₂ O ₃	88 ppm
Nd ₂ O ₃	82 ppm
Pr ₂ O ₃	22 ppm
Sm ₂ O ₃	15 ppm
Dy ₂ O ₃	11.5 ppm
Er ₂ O ₃	6.3 ppm
Ece ₂ O ₃	2.9 ppm
Gd ₂ O ₃	15.0 ppm
Y ₂ O ₃	67.0 ppm
Ga ₂ O ₃	51 ppm
Sc ₂ O ₃	28 ppm

The samples were leached in batch mode at about 150 to about 160° C. for a 6 hour duration with 18.0 wt ° AD HCl+5% excess.

The following extraction yields were measured at the leaching stage.

TABLE 17

Leaching extraction yield measured	
Raw Element	Extraction measured (%)
Al ₂ O ₃	97.9
Fe ₂ O ₃	100
MgO	96.4
Na ₂ O	92.8
K ₂ O	94.0
RE-O incl. Sc and Ga	96.7

After processing through main steps of continuous process, the following yield were measured.

TABLE 18

Global recovery yield	
Element	Global recovery (%)
Al ₂ O ₃	96.20
Fe ₂ O ₃	98.01
MgO	92.64
Na ₂ O	90.77
K ₂ O	93.97
RE/RM-O	90.04

After the ion exchange and solvent for the extraction steps the individual recovery measured for the rare earths and rare metals were:

TABLE 19

Element	Recovery measured (%)
Ga ₂ O ₃	83.58
Sc ₂ O ₃	95.16
Ce ₂ O ₃	93.63
La ₂ O ₃	86.81
Nd ₂ O ₃	91.00
Pr ₂ O ₃	96.00
Sm ₂ O ₃	87.14
Dy ₂ O ₃	93.00
Er ₂ O ₃	91.38
Eu ₂ O ₃	93.83
Gd ₂ O ₃	95.89
Y ₂ O ₃	82.95

From the material balance measured, the consumption of chemical reagents into the solvent extraction were:

Iron powder: 0-Fe₂O₃ removed from hydrolysis;

HCl (32% wt): 0.75 Kg/h as a strip solution ion REE 5× separation and leaching ree oxalates;

Nano water: 10 kg/h for solution strip and washing of precipitation;

Oxalic acid: 325 g/h for precipitation of ree oxalates;

DEHPA 5× solutions: Few grams per hour;

TBP 5× organic solution: 6.5 g/h for gallium records and yttrium separation;

Kerosene: <5 g/h.

[0553] It can thus be inferred from the results shown in Table 15 that the rare earth elements and rare metals extracted present in the obtained leaching composition can eventually be isolated by the processes of the present disclosure such as, for example, those presented in Examples 4 and 5.

[0554] The processes of the present disclosure provide a plurality of important advantages and distinction over the known processes

[0555] The person skilled in the art would understand that processes described in the present disclosure for extracting rare earth elements and rare metals can be used for treating various starting materials. For example, any compositions comprising at least one rare earth element and/or at least one rare earth metal can be used as a starting material. For example, any compositions comprising at least one iron ion and at least one rare earth element can be used as a starting material.

[0556] The person skilled in the art will thus understand that the processes of the present disclosure can be used in combination with various processes for treating aluminum-containing materials, and derivatives, zinc-containing materials and derivatives thereof, copper-containing materials and derivatives thereof, nickel-containing materials and derivatives thereof, magnesium-containing materials and derivatives thereof, and titanium-containing materials.

[0557] In fact, various different treatments can be carried out to the aluminum-containing materials and derivatives, iron-containing materials and derivatives, zinc-containing materials and derivatives thereof, copper-containing materials and derivatives thereof, nickel-containing materials and derivatives thereof, magnesium containing materials and titanium-containing materials and derivatives thereof.

[0558] It was thus shown that the processes of the present disclosure are effective for providing to the existing solutions for extracting rare earth elements. Moreover, it was shown

that such an alternative provided by the processes is an alternative that is a cost effective and environmentally friendly solution.

[0559] While a description was made with particular reference to the specific embodiments, it will be understood that numerous modifications thereto will appear to those skilled in the art. Accordingly, the above description and accompanying drawings should be taken as specific examples and not in a limiting sense.

1-295. (canceled)

296. A process for recovering at least one rare earth element, said process comprising:

obtaining an acidic composition comprising (i) at least one rare earth element and optionally at least one rare metal and (ii) at least one iron ion;

at least partially removing, from said acidic composition, said least one iron ion by means of an extracting agent, an ion exchange resin, hydrolysis and/or by reacting said composition with a reducing agent, thereby obtaining a composition having a reduced content in said at least one iron ion; and

reacting said composition having said reduced content in said at least one iron ion with a precipitating agent so as to substantially selectively precipitate a first rare earth element and optionally a first rare metal that are comprised in a so-formed precipitate, and recovering said precipitate.

297. The process of claim **296**, wherein said acidic composition comprises (i) said at least one rare earth element and optionally said at least one rare metal and (ii) FeCl₃.

298. The process of claim **297**, wherein said extracting agent is chosen from tri-butyl phosphate, di-2-ethylhexyl phosphoric acid (HDEHP), bis(2,4,4-trimethylpentyl) phosphinic acid and 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester).

299. The process of claim **296**, wherein said acidic composition is reacted with Fe(0), thereby obtaining a composition having a reduced content in Fe³⁺.

300. The process of claim **296**, wherein said first rare earth element is scandium.

301. The process of claim **300**, wherein said first rare metal is gallium and said first rare metal is substantially selectively precipitated with said first rare earth element.

302. The process of claim **296**, wherein said precipitating agent is chosen from oxalic acid, NaOH, MgO, CaCO₃ and mixtures thereof.

303. The process of claim **301**, wherein said precipitating agent is chosen from oxalic acid, NaOH, MgO, CaCO₃ and mixtures thereof.

304. The process of claim **301**, wherein said precipitating agent is CaCO₃.

305. The process of claim **304**, wherein said first rare earth element and said first rare metal are substantially selectively precipitated by maintaining a pH value below 2.

306. The process of claim **296**, further comprising leaching said precipitate and obtaining a leaching solution, wherein said leaching solution is further extracted with an extracting agent so as to substantially selectively extract said first rare earth element and said first rare metal and obtain a loaded organic phase.

307. The process of claim **306**, further comprising scrubbing said loaded organic phase with a scrubbing solution so as to recover said first rare earth element and obtained a scrubbed organic phase.

308. The process of any one of claim **307**, further comprising stripping said scrubbed organic phase with a stripping solution so as to recover said first rare metal.

309. The process of claim **296**, wherein said process further comprises, pre-treating or treating said acidic composition with an ion exchange resin so as to remove impurities.

310. The process of claim **302**, wherein said first rare earth element and said first rare metal are substantially selectively precipitated by maintaining Redox potential of about Eh +380 mV.

311. A process for recovering at least one rare earth element, said process comprising:

obtaining an acidic composition comprising (i) at least one rare earth element and at least one rare metal; and (ii) at least one metal ion;

at least partially removing, from said acidic composition, said least one metal ion by means of an extracting agent, an ion exchange resin, hydrolysis and/or by reacting said composition with a reducing agent, thereby obtaining a composition having a reduced content in said at least one metal ion; and

reacting said composition having said reduced content in said at least one metal ion with a precipitating agent so as to substantially selectively precipitate a first rare earth element and a first rare metal.

312. The process of claim **311**, wherein said at least one metal ion comprises at least one aluminum ion, at least one zinc ion, at least one copper ion, at least one nickel ion, at least one magnesium ion, at least one titanium ion and/or at least one iron ion.

313. A process for recovering at least one rare earth element, said process comprising:

obtaining an acidic composition comprising (i) at least one rare earth element and optionally at least one rare metal and (ii) at least one iron ion;

at least partially removing, from said acidic composition, said least one iron ion by means of an extracting agent, an ion exchange resin and/or by reacting said composition with a reducing agent, thereby obtaining a composition having a reduced content in said at least one iron ion; and

reacting said composition having said reduced content in said at least one iron ion with a precipitating agent so as to substantially selectively precipitate a first rare earth element and a first rare metal by maintaining a pH value below 2, wherein said composition having said reduced content in said at least one iron ion being reacted with said precipitating agent so as to obtain a liquid comprising at least one further rare earth element and said precipitate comprising said first rare earth element and said first rare metal, said process further comprising separating said liquid from said precipitate.

314. The process of claim **313**, wherein said first rare earth element and said first rare metal is/are substantially selectively precipitated by maintaining a pH at a value of about 1 to about 2.

315. A process for recovering at least one rare earth element, said process comprising:

obtaining an acidic composition comprising (i) at least one rare earth element and at least one rare metal; and

reacting said composition with a precipitating agent so as to substantially selectively precipitate a first rare earth element and a first rare metal that is gallium.

* * * * *