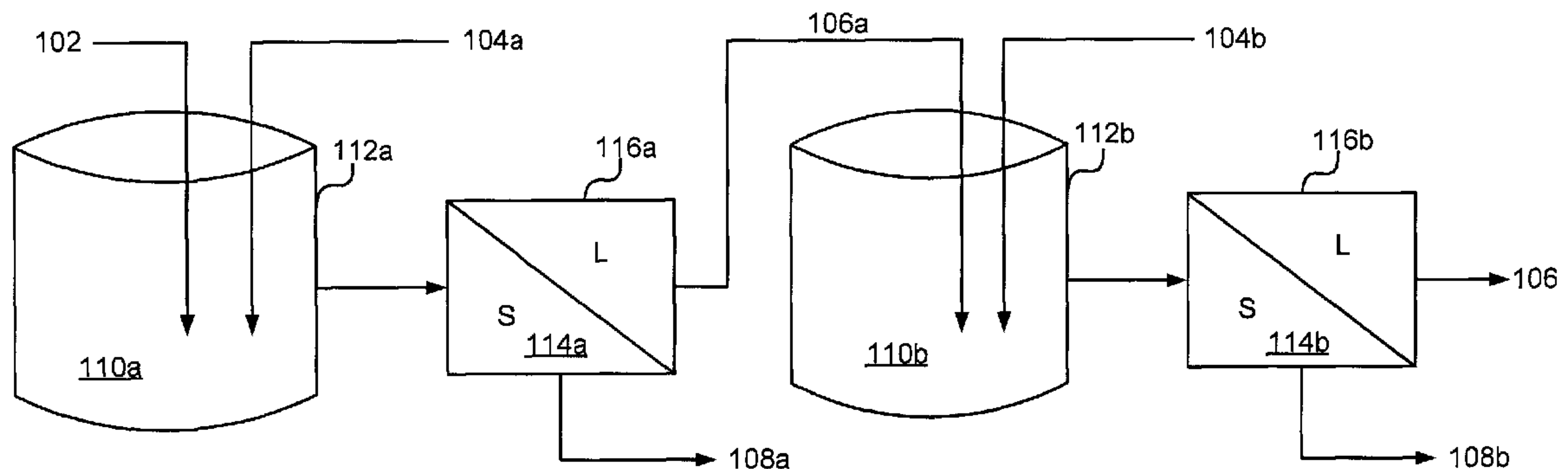




(86) **Date de dépôt PCT/PCT Filing Date:** 2014/01/18
(87) **Date publication PCT/PCT Publication Date:** 2014/07/24
(45) **Date de délivrance/Issue Date:** 2019/02/19
(85) **Entrée phase nationale/National Entry:** 2015/07/17
(86) **N° demande PCT/PCT Application No.:** US 2014/012153
(87) **N° publication PCT/PCT Publication No.:** 2014/113742
(30) **Priorités/Priorities:** 2013/01/18 (US61/754,420);
2013/11/11 (US61/902,579)

(51) **Cl.Int./Int.Cl.** **C22B 3/46** (2006.01),
C22B 3/10 (2006.01), **C22B 3/22** (2006.01),
C22B 59/00 (2006.01)
(72) **Inventeur/Inventor:**
KASAINI, HENRY, US
(73) **Propriétaire/Owner:**
RARE ELEMENT RESOURCES LTD., US
(74) **Agent:** PARLEE MCLAWS LLP

(54) **Titre : EXTRACTION SELECTIVE D'ELEMENTS DE TERRE RARE PAR PRECIPITATION D'ACIDEOXALIQUE**
(54) **Title: SELECTIVE EXTRACTION OF RARE EARTH ELEMENTS BY OXALIC ACID PRECIPITATION**



(57) **Abrégé/Abstract:**

Methods for the extraction of metals such as rare earth metals and thorium from metal compounds and solutions. The methods may include the selective precipitation of rare earth elements from pregnant liquor solutions as rare earth oxalates. The rare earth oxalates are converted to rare earth carbonates in a metathesis reaction before being digested in an acid and treated for the extraction of thorium. A two-step extraction method may be applied to precipitate thorium as thorium hydroxide under controlled pH conditions such that pure thorium precipitate is recovered from a first step and a thorium-free rare earth solution is recovered at the subsequent step. The resulting rare earth solutions are of extremely high purity and may be processed directly in a solvent extraction circuit for the separation of rare earth elements, or may be processed for the direct production of a 99.9% bulk rare earth hydroxide/oxide concentrate.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau(10) International Publication Number
WO 2014/113742 A2(43) International Publication Date
24 July 2014 (24.07.2014)(51) International Patent Classification:
C22B 60/02 (2006.01)(21) International Application Number:
PCT/US2014/012153(22) International Filing Date:
18 January 2014 (18.01.2014)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/754,420 18 January 2013 (18.01.2013) US
61/902,579 11 November 2013 (11.11.2013) US(71) Applicant: RARE ELEMENT RESOURCES LTD.
[US/US]; 225 Union Blvd., Suite 250, Lakewood, CO
80228 (US).(72) Inventor: KASAINI, Henry; 15 Yellow Locust, Littleton,
CO 80127 (US).(74) Agent: DOCKERY, David, F.; Marsh Fischmann & Brey-
fogle LLP, 8055 East Tufts Avenue, Suite 450, Denver,
CO 80237 (US).(81) Designated States (unless otherwise indicated, for every
kind of national protection available): AE, AG, AL, AM,
AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY,BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM,
DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT,
HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR,
KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME,
MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ,
OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA,
SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM,
TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM,
ZW.(84) Designated States (unless otherwise indicated, for every
kind of regional protection available): ARIPO (BW, GH,
GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ,
UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ,
TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK,
EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV,
MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM,
TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW,
KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— of inventorship (Rule 4.17(iv))

Published:

— without international search report and to be republished
upon receipt of that report (Rule 48.2(g))

(54) Title: EXTRACTION OF METALS FROM METALLIC COMPOUNDS

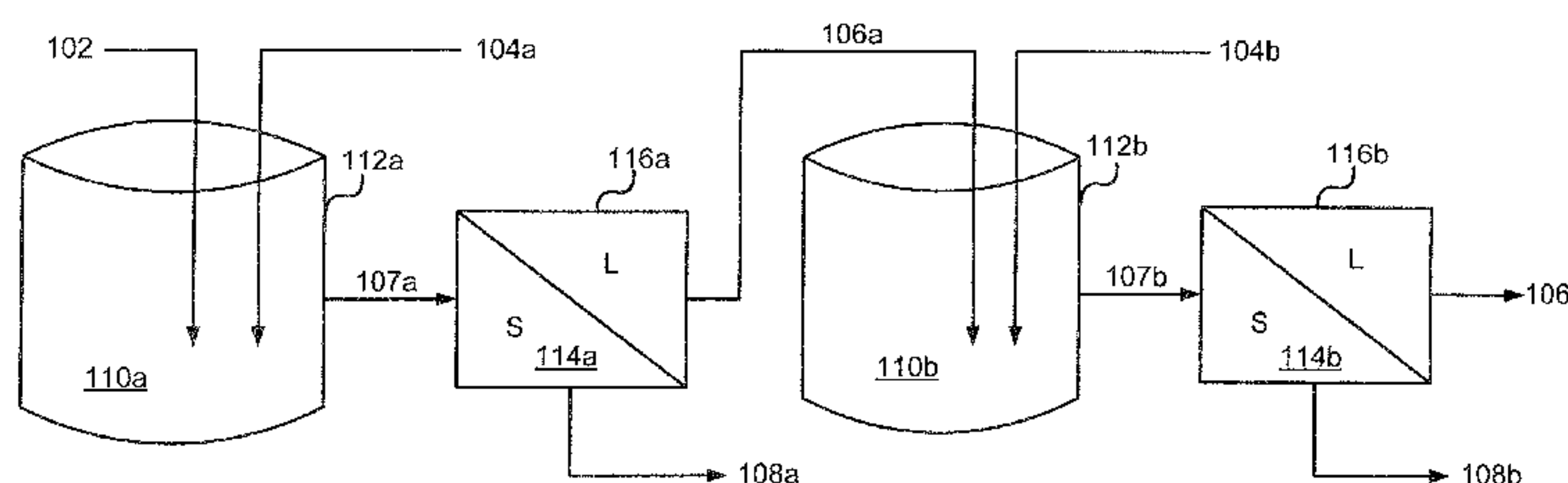


FIG. 2

(57) Abstract: Methods for the extraction of metals such as rare earth metals and thorium from metal compounds and solutions. The methods may include the selective precipitation of rare earth elements from pregnant liquor solutions as rare earth oxalates. The rare earth oxalates are converted to rare earth carbonates in a metathesis reaction before being digested in an acid and treated for the extraction of thorium. A two-step extraction method may be applied to precipitate thorium as thorium hydroxide under controlled pH conditions such that pure thorium precipitate is recovered from a first step and a thorium-free rare earth solution is recovered at the subsequent step. The resulting rare earth solutions are of extremely high purity and may be processed directly in a solvent extraction circuit for the separation of rare earth elements, or may be processed for the direct production of a 99.9% bulk rare earth hydroxide/oxide concentrate.

SELECTIVE EXTRACTION OF RARE EARTH ELEMENTS BY OXALIC ACID PRECIPITATION

[0001] Deleted

FIELD

[0002] This disclosure relates to the field of extractive metallurgy, such as for the extraction of rare earth metals and/or thorium from feedstocks containing these elements.

BACKGROUND

[0003] Rare earth elements (REEs) comprise seventeen elements in the periodic table, specifically the 15 lanthanide elements plus scandium and yttrium. REEs are a group of metallic elements with unique chemical, catalytic, magnetic, metallurgical and phosphorescent properties, and as such find use in a wide variety of modern devices including high-strength magnets, batteries, displays, lighting, and high performance metal alloys.

[0004] REEs are relatively plentiful in the earth's crust. However, REEs are typically highly dispersed and are not often found as concentrated rare earth minerals in economically exploitable ore deposits. The extraction of REEs from mineral deposits is also challenging because mineral deposits containing REEs typically also contain appreciable levels of radioactive elements such as thorium (Th) and uranium (U) that must be safely separated from the REEs during processing of the ore.

[0005] Other ore deposits, such as those containing tantalum (Ta) and/or niobium (Nb), may also contain appreciable amounts of thorium that must be safely removed from the metals during processing of the ore.

SUMMARY

[0006] It is one objective to provide a method for the selective extraction of rare earth elements from base metals by precipitation of pregnant liquor solutions to form rare earth oxalates. The rare earth oxalates may be converted to rare earth carbonates in a metathesis reaction before being digested in an acid and treated for the extraction of thorium.

[0007] It is also an objective to provide a method for the extraction of thorium by precipitating the thorium as thorium hydroxide under controlled pH conditions so that the thorium precipitates without precipitating substantial amounts of rare earth metals. The resulting rare earth solutions are of extremely high purity and may be processed in a solvent extraction circuit for the recovery of high purity rare earth metals, or may be treated to convert the solutions to rare earth oxides.

DESCRIPTION OF THE DRAWINGS

[0008] **Fig. 1** is a schematic flowsheet illustrating a method for the selective precipitation of thorium as thorium hydroxide from an acidic solution.

[0009] **Fig. 2** is a schematic flowsheet illustrating a method for the selective precipitation of thorium as thorium hydroxide from an acidic solution using multiple hydroxylation steps.

[0010] **Fig. 3** is a schematic flowsheet illustrating a method for the precipitation of thorium as thorium hydroxide from an acidic solution including the recycle of acid from a solvent extraction circuit.

[0011] **Fig. 4** is a schematic flowsheet illustrating a method for the precipitation of thorium as thorium hydroxide from an acidic solution including the precipitation of rare earth element hydroxides from a nitric acid solution.

[0012] **Fig. 5** is a schematic flowsheet illustrating a method for the conversion of a rare earth oxalate product to a rare earth carbonate product by metathesis.

[0013] **Fig. 6** is a schematic flowsheet illustrating a method for the conversion of a rare earth oxalate product to a rare earth carbonate product by metathesis including the recycle of acid from a solvent extraction circuit.

[0014] **Fig. 7** is a schematic flowsheet illustrating a method for the precipitation of rare earth elements as rare earth oxalates from a pregnant liquor solution.

[0015] **Fig. 8** is a schematic flowsheet illustrating a method for leaching a rare earth ore concentrate to form a pregnant liquor solution.

[0016] **Figs. 9A and 9B** are flowsheets illustrating comprehensive methods for the extraction of rare earth elements from an ore incorporating various embodiments of the present disclosure.

[0017] **Figs. 10A and 10B** illustrate the effect of pH on selective thorium precipitation when using a hydroxide precipitant to precipitate thorium as thorium hydroxide.

DESCRIPTION OF THE EMBODIMENTS

[0018] In some embodiments, the present disclosure relates to methods for the selective precipitation of thorium (Th) from acidic solutions of metals, such as acidic solutions containing rare earth elements ("REEs"), such as an acidic solution that is derived from a pregnant liquor solution ("PLS") formed by acid leaching of an ore (*e.g.*, a mineral ore concentrate) containing the REEs. In some embodiments, the present disclosure relates to methods for preparing the acidic solutions, such as from rare earth oxalates (REE-oxalates) or other rare earth compounds, which may be derived from a mineral ore. In some embodiments, the present disclosure relates to methods for the precipitation of REEs from a solution (*e.g.*, a PLS) in the form of REE-oxalates. In other embodiments, the present disclosure relates to unique products that may be formed by the disclosed methods when applied alone or in combination.

[0019] REEs comprise 17 elements in the periodic table, namely the 15 lanthanide elements plus scandium and yttrium. Specifically, the REEs include scandium (Sc), yttrium (Y), lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb),

dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), and lutetium (Lu). All of these REEs except Pm are found in nature, *e.g.*, in mineral deposits. Many REEs find use in modern devices and have a very high value do to their relative scarcity. Of particularly high value are the REEs yttrium, praseodymium, neodymium, europium, terbium and dysprosium.

[0020] Many mineral deposits containing REEs also contain radioactive elements, such as thorium and uranium. Radioactive elements may also be found with other non-REE mineral deposits, such as uranium deposits, tantalum deposits and niobium deposits. It is highly desirable to separate these radioactive elements from the non-radioactive metals before final processing to extract the non-radioactive metals, *e.g.*, from a solution of the non-radioactive metals.

[0021] In a first embodiment, a method for the selective precipitation of thorium from an acidic solution containing solubilized thorium is provided. The method may be applicable to solutions that contain other solubilized metals in addition to the thorium, such as solubilized REEs, uranium, tantalum or niobium. In one example, the acidic solution includes significant amounts of solubilized REEs (*i.e.*, an acidic REE solution), such as an acidic solution that is derived from a rare earth ore concentrate. In one particular example, the acidic solution includes one or more of yttrium, praseodymium, neodymium, europium, terbium and dysprosium. Although the following description primarily describes the extraction of thorium from such acidic REE solutions, the thorium precipitation method of this embodiment may be applicable to other acidic solutions containing solubilized thorium, such as acidic solutions containing Group 5 metals such as tantalum and/or niobium.

[0022] The method of this embodiment includes the precipitation of thorium in the form of thorium hydroxide (*e.g.*, $\text{Th}(\text{OH})_3$ or $\text{ThO}(\text{OH})_3$) from an acidic solution. For example, the method may include precipitating thorium as thorium hydroxide by contacting the acidic solution with a hydroxide precipitant, *e.g.*, by contacting the acidic solution with a compound that includes a hydroxide group, such as sodium hydroxide (NaOH) and/or ammonium hydroxide (NH_4OH). Thorium hydroxide may be precipitated from the acidic solution while maintaining a substantial portion of other valuable metals

(e.g., REEs) in solution for subsequent recovery of the other metals, such as in a solvent extraction circuit. In one example, the acidic solution may have a relatively low free acid content, such as about 5 g/l (grams per liter) of acid.

[0023] **Fig. 1** illustrates a schematic flowsheet of a method for the precipitation of thorium from an acidic solution according to this embodiment. As illustrated in **Fig. 1**, an acidic solution **102** containing at least solubilized thorium is contacted with a hydroxide precipitant **104** in a hydroxylation step **110**, e.g., by contacting the acidic solution **102** and the hydroxide precipitant **104** in a reactor **112** to cause thorium in the acidic solution **102** to precipitate as thorium hydroxide. After at least a portion of thorium in the acidic solution **102** has precipitated from the acidic solution **102** as thorium hydroxide, a thorium depleted solution **106** may be separated from a thorium hydroxide product **108** in a separating step **114**, e.g., using a filter **116**.

[0024] The acidic solution **102** contains at least solubilized thorium. As is discussed in more detail below, the acidic solution **102** may be derived from the leaching of a mineral ore (e.g., an ore concentrate) containing REEs or other high-value metals. Thorium is among the elements that are commonly found in mineral deposits containing REEs and the resulting acidic leach solutions typically contain undesirable concentrations of thorium. In one example of this embodiment, the concentration of solubilized thorium in the acidic solution **102** is at least about 50 mg/l (milligrams per liter), such as at least about 100 mg/l of solubilized thorium in the acidic solution **102**, or even at least about 200 mg/l of solubilized thorium.

[0025] The acidic solution **102** may also include one or more REEs, i.e., REEs that are also solubilized in the acidic solution **102**. For example, the acidic solution **102** may include REEs in a concentration of at least about 10 grams per liter (g/l). In certain characterizations, the acidic solution **102** includes a relatively high concentration of REEs, such as at least about 15 g/l REEs, at least about 20 g/l REEs, at least about 30 g/l or even at least about 50 g/l REEs, where the REEs are solubilized (e.g., dissolved) into the acidic solution **102**. Typically, the acidic solution **102** will include not greater than about 100 g/l REEs. In one particular characterization of this example, the acidic

solution **102** includes at least one or more REEs of particularly high value, such as one or more of praseodymium, neodymium, europium, terbium and dysprosium.

[0026] The solution **102** is acidic and may have a pH of not greater than about pH 3.8, such as not greater than about pH 4.2, prior to being contacted with the hydroxide precipitant **104**. In one example, the acidic solution includes nitric acid (HNO_3), although other acids such as sulfuric acid (H_2SO_4) may also be useful in the embodiments disclosed herein. For example, the acidic solution **102** may comprise nitric acid (HNO_3) and may be obtained from the acid digestion of rare earth compounds, e.g., the acid digestion of earth oxide (RE-oxides), rare earth hydroxides (RE-hydroxides), rare earth oxalates (RE-oxalates) and/or rare earth carbonates (RE-carbonates) with nitric acid to form solubilized nitrate compounds of REEs. Nitric acid is particularly useful, as the thorium hydroxide precipitated during hydroxylation **110** will become stable and thus will not dissolve, even at a relatively low pH.

[0027] The acidic solution **102** comprises nitric acid, and in one particular example, the acidic solution **102** has a free acid concentration in the range of from about 0.5 g/l to about 55 g/l HNO_3 . When the acidic solution **102** comprises nitric acid, the solubilized elements (e.g., thorium and REEs) may be in the form of solubilized nitrate salts. It is an advantage of this embodiment that the acidic solution **102** may have a relatively low free acid concentration, and therefore may require relatively small quantities of the hydroxide precipitant **104** to precipitate thorium hydroxide and to avoid diluting metal species in solution, which favors crystallization to precipitate thorium.

[0028] The acidic solution **102** may also include traces of non-REE elements that are solubilized in the acidic solution **102**. For example, the non-REE elements may include metallic elements, such as: alkali metals such as sodium (Na) and potassium (K); alkaline earth metals such as magnesium (Mg), calcium (Ca), strontium (Sr) and barium (Ba); transition metals such as nickel (Ni), copper (Cu), zirconium (Zr), iron (Fe), manganese (Mn) and titanium (Ti); post-transition metals such as lead (Pb) and aluminum (Al); metalloids such as silicon (Si); and radioactive metals (e.g., actinides) such as thorium (Th) and uranium (U). The non-REE elements may also include non-metallic elements such as sulfur (S) and phosphorous (P).

[0029] In one example, however, the acidic solution **102** includes primarily REEs and thorium, with little or no other non-REE elements (*e.g.*, base metals) that are solubilized in the acidic solution **102**. For example, the acidic solution **102** may comprise not greater than about 5 wt.% non-REE elements, such as not greater than about 3 wt.% non-REE elements. Method for the formation of such acidic solutions are described in more detail below.

[0030] The hydroxylation step **110** includes contacting the acidic solution **102** with a hydroxide precipitant **104**, such as sodium hydroxide or ammonium hydroxide, to precipitate a thorium hydroxide product **108** (*e.g.*, predominately containing particulate thorium hydroxide). For example, the reactants may be contacted in a reactor **112** under conditions such that at least a portion of the thorium solubilized in the acidic solution **102** precipitates as a thorium hydroxide product **108**.

[0031] It is an advantage of the method of this embodiment that the thorium may be precipitated from the acidic solution **102**, while a substantial majority of the REEs contained in the acidic solution **102** remain solubilized in a thorium depleted solution **106** that is separated from the thorium hydroxide product **108**. To ensure that sufficient quantities of thorium precipitate from the acidic solution **102** and that a substantial majority of REEs in the acidic solution **102** remains solubilized, it has been found that the pH during the hydroxylation step **110** should be maintained at a pH that enables high selectivity for thorium, *i.e.*, to preferentially precipitate thorium from the acidic solution **102**. In one characterization, the pH during the hydroxylation step **110** is within the range of at least about pH 3 and not greater than about pH 4. It has been found that increasing the pH within this range may increase the amount of thorium precipitated from the acidic solution **102** as a thorium hydroxide product **108**. In one characterization, the pH during the hydroxylation step **110** is maintained at a pH of at least about pH 3.0, such as at least about pH 3.1, at least about pH 3.2, at least about pH 3.3, at least about pH 3.4 or even at least about pH 3.5, such a at least about pH 3.6. However, as the pH approaches about pH 4, an increasing quantity of REEs may also precipitate from the acidic solution **102** (*e.g.*, as particulate REE-hydroxides). In the embodiment illustrated in **Fig. 1**, to avoid the precipitation of undesirable quantities

of REEs from the solution, the pH should be maintained at less than pH 4, such as not greater than pH 3.9 or not greater than pH 3.8. In one example, the pH during the hydroxylation step **110** may be maintained at the desired pH level by controlling the quantity of hydroxide precipitant **104** that is added to the reactor **112** during the hydroxylation step **110**, e.g., during the precipitation of thorium from the acidic solution **102**.

[0032] It has also been found that the desirable range of pH values for the selective precipitation of thorium is dependent upon the concentration of solubilized thorium in the acidic solution **102**. In particular, it has been found that increased pH values within the range of about pH 3.5 to pH 4 may be utilized to selectively precipitate thorium as a thorium hydroxide product **108** without precipitating significant amounts of REEs when the concentration of thorium in the acidic solution **102** is relatively low. That is, as the concentration of the thorium in the acidic solution **102** decreases, the pH during the hydroxylation step **110** may be increased to remove additional thorium without removing undesirable quantities of REEs. In one example, the acidic solution **102** can be diluted (e.g., with water) to reduce the thorium concentration, and the hydroxylation step **110** may be carried out at a higher pH (e.g., pH 3.5 to pH 3.9) without precipitating undesirable quantities of REEs. In one characterization, the acidic solution **102** comprises not greater than about 800 mg/l of thorium, such as not greater than 500 mg/l, or even not greater than about 200 mg/l thorium, and the contacting step is carried out at a pH of at least about pH 3.5, such as at least about pH 3.6, at least about pH 3.7, and even at least about pH 3.8, but not greater than pH 4, such as not greater than pH 3.9. However, it is believed that at least about 50 mg/l of thorium is required in the solution for precipitation of thorium to occur.

[0033] The acidic solution **102** and the hydroxide precipitant **104** should remain in contact (e.g., in reactor **112**) for a period of time sufficient to precipitate a majority (e.g., at least about 50%) of the thorium from the acidic solution **102** and form a thorium depleted solution **106** and a thorium hydroxide product **108**. In one characterization, the time of contact (e.g., the average residence time in the reactor) during the hydroxylation step **110** may be at least about 30 minutes and may be not greater than about 90

minutes. It is an advantage of this embodiment that the hydroxylation step **110** may be carried out at ambient temperatures, *e.g.*, the step does not typically require the reactor **112** to be heated or cooled. Further, the hydroxylation step **110** may be carried out at ambient pressures, *e.g.*, the step does not require a sealed or otherwise pressure-controlled reactor **112**.

[0034] After the contacting step **110**, the thorium hydroxide product **108** may be separated from the thorium depleted solution **106** in a separating step **114**. For example, a filter **116** may be used to filter the output stream **107** containing thorium hydroxide and the thorium depleted solution **106** from the reactor **112** and retain the thorium hydroxide product **108** on the filter **116**. The thorium depleted solution **106** (*i.e.*, the filtrate), containing high levels of REEs and very low levels of thorium, may be further treated as is discussed below. The thorium hydroxide product **108** may advantageously be of high purity, *i.e.*, the product may comprise at least about 99 wt. % thorium hydroxide, such as at least about 99.9 wt.% thorium hydroxide. The thorium hydroxide product **108** may be disposed of, or may be a salable commodity particularly in view the high purity of the thorium hydroxide product **108**.

[0035] As is noted above, thorium precipitation from the acidic solution may be enhanced with increased pH (*e.g.*, up to about pH 4) and with a decreased concentration of thorium in the acidic solution and with low free acid content. In one example of this embodiment, this finding may be applied in a multi-step (*e.g.*, two-step) process. Specifically, the thorium extraction method of this embodiment may include a first hydroxylation step that includes contacting an acidic solution with a hydroxide precipitant at a first pH, *e.g.*, of at least about pH 3 and not greater than about pH 4, to precipitate a thorium hydroxide product containing very low amounts of REEs and form an intermediate thorium depleted solution, *i.e.*, having a lower concentration of thorium than the acidic solution. The intermediate thorium depleted solution may then be subjected to a second hydroxylation step where the intermediate thorium depleted solution is contacted with a hydroxide precipitant at a second pH of at least about pH 3.1 and not greater than about pH 4.2, where the second pH is greater than the first pH to remove additional thorium. In one particular characterization of this method, the pH

during the first hydroxylation step is from about pH 3.0 to about pH 3.3, and the pH during a second hydroxylation step is from about pH 3.5 to about pH 4. In this regard, the pH in the second hydroxylation step may be carried out at such higher pH to aggressively remove thorium, even in the event some REEs may precipitate with the thorium hydroxide product, as is discussed below.

[0036] In this embodiment, some additional solubilized thorium is precipitated as thorium hydroxide in the second hydroxylation step to form a thorium depleted solution, *i.e.*, having a lower concentration of thorium than the intermediate thorium depleted solution, and that also has a relatively high concentration of REEs in solution. As compared to the embodiment described with respect to **Fig. 1**, the thorium depleted solution from the second hydroxylation step may be recycled to the first hydroxylation step so that only small concentrations of REEs report with the thorium hydroxide product.

[0037] Referring now to **Fig. 2**, this exemplary method may include a first hydroxylation step **110a** where the acidic solution **102** is contacted with a first hydroxide precipitant **104a**, such as in a first reactor **112a**, under conditions such that at least a portion of the thorium in the acidic solution **102** precipitates as a first thorium hydroxide product **108a** and a substantial majority of the REEs (*e.g.*, at least about 99 at.% of the REEs) remain solubilized in an intermediate thorium depleted acidic solution **106a**. For example, at least about 50 at.% of the thorium in the acidic solution **102** may be precipitated in reactor **112a** and removed in a first separation step **114a**, *e.g.*, using a filter **116a**. In one particular characterization, at least about 60 at.% and not greater than about 90 at. % of the thorium in the acidic solution **102** is separated from the intermediate thorium depleted solution **106a** in the separation step **114a** as a thorium hydroxide product **108a**. As a result, the intermediate thorium depleted solution **106a** recovered from the separation step **114a** has a lower concentration of thorium than the acidic solution **102**.

[0038] As is discussed above, the lower concentration of thorium in the intermediate thorium depleted solution **106a** advantageously enables a higher pH to be utilized in a second hydroxylation step **110b** (*i.e.*, as compared to the first hydroxylation step **110a**),

e.g., in a second reactor **112b**. Thus, in a second separation step **114b**, a second thorium hydroxide product **108b** is separated from the thorium depleted solution **106**. The thorium depleted solution **106** from the separation step **114b** may advantageously include not greater than about 5% of thorium contained in the acidic solution **102**, such as not greater than about 2% of the thorium contained in the acidic solution **102**. Further, due to the high selectivity of the process, at least about 95%, such as at least about 98%, of REEs in the acidic solution **102** may remain solubilized in the thorium depleted solution **106**. Although illustrated as a two-step process in **Fig. 2** (*e.g.*, including two hydroxylation steps), the method may include additional incremental steps if desired for enhanced thorium precipitation and/or enhanced REE recovery.

[0039] Further, the amount of thorium hydroxide product **108b** that is separated from the thorium depleted solution **106** may be relatively small, as compared to the amount of thorium hydroxide product **108a** that is separated from the intermediate thorium depleted solution **106a**. Further, the thorium hydroxide product **108b** may include some REEs (due to the higher pH used in hydroxylation step **110b**). In one characterization, the thorium hydroxide product **108b** may include up to about 20 at.% REEs on a metals basis. Therefore, in one example, the thorium hydroxide product **108b** may be recycled back to the first hydroxylation step **110a**, so that the recovery of REEs in the thorium depleted solution **106** is increased. That is, any increase in the amount of REEs precipitated as REE-hydroxides in hydroxylation step **110b** may be mitigated by recycling the thorium hydroxide product **108b** to hydroxylation step **110a**, keeping the REEs in the circuit. Thus, in this example, all of the thorium hydroxide may be extracted from the circuit with the thorium hydroxide product **108a**.

[0040] In one example of the foregoing embodiments, ammonium hydroxide is utilized as a hydroxide precipitant **104/104a/104b** to precipitate thorium as thorium hydroxide. For example, ammonium hydroxide may be added as an aqueous solution having a concentration of from about 10% to about 20% ammonium hydroxide, *e.g.*, about 15%. As a result, the thorium depleted solution **106** recovered from the separation step(s) **114** will contain substantial amounts of ammonium nitrate (NH_4NO_3), dissolved in the thorium depleted solution **106**. As is discussed in more detail below, it

may be desirable to continuously or intermittently extract the ammonium nitrate, which is a valuable and salable by-product.

[0041] In some embodiments of the present disclosure, methods for the formation of the acidic solution are provided. Further, methods for the extraction of REEs from the thorium depleted solution are provided. In some examples, it may be advantageous to integrate the method(s) described above for the precipitation of thorium from an acidic solution with a solvent extraction circuit for extracting REEs from the thorium depleted solution. It may also be advantageous to integrate a method for the formation of the acidic solution, before hydroxylation, by acid digestion of rare earth compounds, particularly acid digestion of REE-carbonates. In one particular embodiment, reagent consumption may be reduced and overall operating expenses of the process reduced by recycling nitric acid from a solvent extraction circuit to an acid digestion step to form the above-described acidic solution. In one characterization, nitric acid consumption may be reduced to almost zero, with only make-up nitric acid being added to the process to compensate for normal evaporation and leakage losses.

[0042] In one example, the acidic solution is formed by the acid digestion of an REE-carbonate product, such as one that has a high purity with respect to REEs. As illustrated in **Fig. 3**, an REE-carbonate product **174** may be contacted with an acid **120** (e.g., fresh nitric acid or sulfuric acid) in an acid digestion step **122**, such as in a reactor **124**. The resulting acidic solution **102** may be an acidic solution substantially as described above with respect to **Figs. 1** and **2**. The acidic solution **102** may be contacted in a first hydroxylation step **110a** with a hydroxide precipitant **104a** to precipitate a thorium hydroxide product **108a** from the acidic solution **102**. The thorium hydroxide product **108a** may be separated from the thorium depleted solution **106b** in a separation step **114a**. Thereafter, as illustrated with respect to **Fig. 2**, the intermediate thorium depleted solution **106b** may be contacted in a second hydroxylation step **110b** with a second hydroxide precipitant **104b** to form the thorium depleted solution **106**. The thorium depleted solution **106** may then be separated from the second thorium hydroxide product **108b** in a separation step **114b**.

[0043] As is noted above, the amount of thorium hydroxide product **108b** may be relatively small and there may be appreciable quantities of REEs in the thorium hydroxide product **108b**. To reduce losses of REEs, the thorium hydroxide product **108b** may be recycled back to the process, and as illustrated in **Fig. 3**, the second thorium hydroxide product **108b** is recycled back to the acid digestion step **122** where the thorium is re-digested with the REE-carbonate product **174**. In this manner, all of the thorium hydroxide is removed from the acidic solution **102** with the first thorium hydroxide product **108a**. When the thorium hydroxide product **108b** is separated in separating step **114b**, the resulting thorium depleted solution **106** is a relatively high purity REE-nitrate solution.

[0044] The high purity REE-nitrate solution **106** may then be subjected to a solvent extraction circuit **126** to extract REEs from the thorium depleted solution **106**. It is an advantage of this embodiment that having the REEs solubilized in nitrate media may reduce the expenses associated with a solvent extraction circuit. The solvent extraction circuit **126** may include the steps of solvent extraction **128** and solvent stripping **130** with a stripping solvent **132**. Solvent extraction circuits for the recovery of REEs are known in the art and will not be described here in additional detail. However, because the thorium depleted solution **106** described herein is of extremely high purity, the solvent extraction circuit **126** may advantageously be operated at a reduced capital expense and reduced operating expense. The resulting products are very high purity and high value REEs **134**.

[0045] As is noted above, the thorium depleted solution **106** may include substantial quantities of highly salable ammonium nitrate. Thus, an ammonium nitrate removal step **136** may be utilized to continuously or intermittently remove ammonium nitrate **138** from the solution **106**. As illustrated in **Fig. 3**, the ammonium nitrate is removed after the solvent extraction circuit **126**, as the presence of ammonium nitrate in the thorium depleted solution **106** is not believed to impair the efficacy of the solvent extraction circuit **126**. However, it will be appreciated that the ammonium nitrate separation step may also occur before the solvent extraction circuit **126** if desired.

[0046] The ammonium nitrate separation step **136** may include cooling the thorium depleted solution to a reduced temperature (e.g., below about 10°C) to crystallize ammonium nitrate **138**. Because ammonium nitrate **138** is highly soluble in acid, it may only be necessary to intermittently operate the separation step **136** to remove ammonium nitrate **138**. Ammonium nitrate is valuable and salable by-product that is widely used in the fertilizer industry and may represent a significant source of revenue from the process.

[0047] As illustrated in **Fig. 3**, after separation of the ammonium nitrate **138** (intermittently or continuously), the nitric acid **140** (e.g., recycled nitric acid) may be recycled back to the process, e.g., back to the acid digestion step **122**. Thus, the acid (e.g., input at **120**) may be contained in an essentially "closed loop" within the process. Additional nitric acid may be generated during the solvent extraction circuit due to cationic ion exchange releasing protons into solution. In this regard, a substantial quantity of the nitric acid required for the acid digestion step may be provided by the recycled nitric acid **140**, and only a small amount of fresh nitric acid **120** may be required for the process once steady state and continuous operations are achieved and maintained.

[0048] **Fig. 3** illustrates the integration of a solvent extraction circuit for the extraction of high purity REEs as metals from the nitrate solution containing the REEs. In other embodiments, it may be advantageous to integrate the method(s) described herein for the precipitation of thorium from an acidic solution with a circuit for precipitating the REEs, e.g., as REE-oxides and/or REE-hydroxides.

[0049] In this regard, **Fig. 4** illustrates an example of an integrated process similar to the process illustrated in **Fig. 3**, but where an REE precipitation circuit replaces the solvent extraction circuit of **Fig. 3**. Thus, the thorium depleted and REE-nitrate rich solution can be treated to precipitate high purity REE-compounds such as REE-oxides and/or REE-hydroxides which, for example, may be shipped to a separate facility for extraction of the REEs as metals.

[0050] Referring to **Fig. 4**, the thorium depleted solution **106** from the separation step **114b** will typically have a pH in the range of about pH 3.6 to about pH 4 (e.g.,

about pH 3.8) and will be rich in REE-nitrates and may contain no, or extremely low levels of, thorium and/or uranium. For example, the solution **106** may include not greater than about 1 ppm thorium and/or uranium. As illustrated in **Fig. 4**, this solution **106** is conveyed to an REE precipitation step **142**, where the solution **106** is contacted with an REE precipitation agent **144**. In one characterization, ammonium hydroxide is used for precipitation in both the precipitation step **144** to precipitate REEs and in the hydroxylation step(s) **110a/110b** to precipitate thorium. The REE precipitation agent **144** may be added to the solution **106** in sufficient quantities to increase the pH of the solution, such as by increasing the pH to at least about pH 4.5, such as at least about pH 4.9. In one characterization, the pH during the precipitation step **144** is not greater than about pH 6 and may be about pH 5.5. At these pH levels, the REEs will precipitate from the solution **106** as REE-hydroxides **146**, which may be separated from an REE-depleted nitrate solution **148** in a separation step **150**.

[0051] The REE-hydroxides **146** may then be converted from the REE-hydroxides to REE-oxides. As illustrated in **Fig. 4**, the REE-hydroxides **146** are conveyed to a drying step **152** where the REE-hydroxides are heated to a drying temperature that is sufficient to convert a substantial majority of the REE-hydroxides **146** to REE-oxides **154**. For example, the drying step **152** may include heating the REE-hydroxides **146** to a temperature of at least about 100°C, such as at least about 120°C, and not greater than about 160°C, such as not greater than about 150°C. In one example, the REE-hydroxides **146** are conveyed to a screw feed dryer for the substantially continuous production of the REE-oxides **154**. In another example, the REE-hydroxides **146** may be stockpiled as necessary and dried batchwise.

[0052] It is an advantage of this embodiment that the resulting REE-oxide product **154** will have a very high purity, particularly with respect to base metals and radioactive metals such as uranium and thorium. In one example, the REE-oxide product **154** has a purity of at least about 99.8%, *i.e.*, the REE-oxide product **154** comprises at least about 99.8% REE-oxides, such as a purity of at least about 99.9%. For example, the REE-oxide product **154** may comprise not greater than about 1 ppm thorium. The

uranium content may be not greater than 0.1 ppm, for example, such a not greater than about 0.01 ppm.

[0053] An REE-depleted nitrate solution **148** may also recovered from the separation step **150**, and may have a high content of ammonium nitrate, such as from about 30 g/l to about 50 g/l ammonium nitrate. The solution **148** may be recycled to preserve nitrates and in particular to preserve ammonium in the process. As illustrated in **Fig. 4**, the REE-depleted nitrate solution **148** may be conveyed to a vessel **156** where ammonium hydroxide is stored for use in the process, *i.e.*, where the recycled nitrate solution **148** is added to fresh ammonium hydroxide **158**. An ammonium hydroxide product **160** such as an ammonium hydroxide solution may then be conveyed as needed to the process, *e.g.*, to hydroxylation steps **110a/110b** and/or to REE precipitation step **142**. Because the recycled REE-depleted nitrate solution will contain ammonium nitrates, it may be desirable to remove the ammonium nitrates from the ammonium hydroxide vessel **156** on a continuous or intermittent basis. In this regard, a portion **162** of the solution contained within vessel **156** may be periodically bled off from the vessel **156** and subjected to an ammonium nitrate precipitation step **164** to crystallize an ammonium nitrate by-product **166** and recycle an ammonium nitrate depleted solution **168** back to the vessel **156**. The ammonium nitrate by-product **166** will be of high purity and a valuable by-product of the process.

[0054] While one example for the precipitation of REE compounds from the thorium depleted solution have been described in detail, it will appreciated that other methods may be applied. For example, in some examples, it may be desirable to directly precipitate the REEs as REE-nitrates from the thorium depleted solution.

[0055] As is noted above, the acidic solution **102** may contain REEs in addition to thorium, and may be formed by the dissolution of a variety of compounds in an acid (*e.g.*, dissolution by acid digestion). In some of the embodiments disclosed herein, it is desirable that the REEs are in the form of REE-oxalates, *e.g.*, $RE_2(C_2O_4)_3$ or $RE_3(C_2O_4)_3$, where RE is a rare earth element. However, the solubility of REE-oxalates in acid is very low. Thus, in one example, the acidic solution **102** is formed by the dissolution of carbonate compounds, such as $RE_2(CO_3)_3 \cdot xH_2O$ where RE is a rare earth

element, and $\text{Th}(\text{CO}_3)_2 \cdot x\text{H}_2\text{O}$, as illustrated above in **Fig. 3**. The REE-carbonates may be formed by a variety of methods, and in one example the REE-carbonates are formed from REE-oxalates by a metathesis reaction to render the REEs soluble in an acid such as nitric acid.

[0056] In the embodiment illustrated in **Fig. 5**, an REE-oxalate product **170** is converted in a metathesis step **172** to a REE-carbonate product **174** for subsequent dissolution of the REE-carbonate product **174** in an acid, e.g., to solubilize the REEs and thorium in an acidic solution **102** (**Fig. 3**). In this embodiment, an REE-oxalate product **170** is contacted with a carbonate compound **176** such as sodium carbonate (Na_2CO_3) in the metathesis step **172**, along with a solvent **178** such as water, which may be introduced with the other reactants or introduced separately. For example, the metathesis step **172** may include contacting the reactants in a reactor **180** for a period of time sufficient to convert at least about 98%, such as at least about 98.5% of the REEs in the REE-oxalate product **170** to REE-carbonates in the REE-carbonate product **174**. Similarly, the metathesis step **172** may be carried out for a period of time sufficient to convert at least about 98%, such as at least about 98.5% of thorium in the REE-oxalate product **170** from thorium oxalate to thorium carbonate in the REE-carbonate product **174**. The only by-product of the metathesis step **172** is a high-purity carbon dioxide stream **182** which may be captured as a by-product.

[0057] In a separation step **184**, the REE-carbonate product **174** (e.g., REE-carbonate particulates) may be separated from an oxalate solution **186** such as by using a filter **188**. The oxalate solution **186** will include substantial amounts of dissolved oxalates (e.g., $\text{Na}_2\text{C}_2\text{O}_4 \cdot y\text{H}_2\text{O}$ when the carbonate compound **176** is sodium carbonate) and in some examples discussed below, the oxalate solution **186** may advantageously be recycled to a step where REEs are precipitated as the REE-oxalate product **170**.

[0058] Another embodiment of the present disclosure is directed to the integration of several of the above-described methods in a process for extracting REEs from an REE-oxalate product by applying a metathesis reaction to convert the REE-oxalates to REE-carbonates, digesting the REE-carbonates in an acid to form an REE-rich solution, and selectively precipitating thorium from the REE-rich solution. The resulting high purity

REE-nitrate solution may then be treated in a solvent extraction circuit to extract the REEs, or may be processed to recover a dry powder of REE-nitrates, REE-oxides or REE-hydroxides.

[0059] As illustrated in **Fig. 6**, a metathesis step **172** may be carried out by contacting an REE-oxalate product **170** and a carbonate compound **176** such as sodium carbonate in a reactor to form an REE-carbonate product **174** and an oxalate solution **186**, e.g., an oxalate solution containing dissolved sodium carbonate. The REE-carbonate product **174** is then subjected to an acid digestion step **122** where the REE-carbonate product **174** may be contacted with nitric acid, e.g., fresh nitric acid **120** and/or recycled nitric acid **140** such as from a subsequent solvent extraction circuit **126**. Recycled thorium hydroxide product **108b** from a downstream hydroxylation step **110b** may also be added to the acid digestion step **122**.

[0060] The resulting acidic solution **102** containing dissolved carbonates may then be subjected to hydroxylation in steps **110a** and **110b** to form a thorium hydroxide product **108a** which is a high purity thorium hydroxide product containing very small concentrations of REEs. The thorium depleted solution **106** may then be separated from the thorium hydroxide product **108b** and subjected to a solvent extraction circuit **126** to extract REEs therefrom, as is described with respect to **Fig. 4**. The REE-depleted nitrate solution **148** may be recycled, e.g., also as described with respect to **Fig. 4**.

[0061] In another embodiment of this disclosure, a method for the formation of REE-oxalates from a solution, such as a pregnant liquor solution ("PLS") is provided. The method may include the extraction of the REEs from a PLS in the form of a precipitation product that includes REE-oxalate particulates. In accordance with this embodiment, the precipitation of oxalate compounds (e.g., REE-oxalates) from a PLS containing REEs and other elements (e.g., base metals, uranium and other metals) advantageously may result in a very high purity REE-oxalate product having a very low concentration of non-REE elements. Further, certain embodiments provide for the recycling of oxalic acid and/or oxalate compounds to reduce the overall consumption of oxalic acid by the process.

[0062] **Fig. 7** schematically illustrates one such method for the formation of an REE-oxalate product having low concentrations of non-REE elements. As illustrated in **Fig. 7**, a PLS **190** is contacted with oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) **192** in an oxalate formation step **194**. The PLS **190** may include one or more REEs, *i.e.*, REEs that have been dissolved (*e.g.*, solubilized) in the PLS **190**. For example, the PLS **190** may be an acidic solution (*e.g.*, from a chloride leach) and the REEs may be present as dissolved salts, such as dissolved chloride salts. In one example, the PLS **190** includes a concentration of REEs of at least about 20 g/l. For example, the PLS **190** may include at least about 25 g/l REEs, such as at least about 30 g/l REEs, at least about 35 g/l REEs, or even at least about 40 g/l REEs.

[0063] The PLS **190** may also include non-REE elements that are solubilized in the PLS **190**. The non-REE elements may include metallic elements, particularly: alkali metals such as sodium (Na) and potassium (K); alkaline earth metals such as magnesium (Mg), calcium (Ca), strontium (Sr) and barium (Ba); transition metals such as nickel (Ni), copper (Cu), zirconium (Zr), iron (Fe), manganese (Mn) and titanium (Ti); post-transition metals such as lead (Pb) and aluminum (Al); metalloids such as silicon (Si); and radioactive metals (*e.g.*, actinides) such as thorium (Th) and uranium (U). The non-REE elements may also include non-metallic elements such as sulfur (S) and phosphorous (P). Among the foregoing, and in certain characterizations, the PLS **190** may particularly include Mn in concentrations of at least about 10 g/l and/or may include Fe in concentrations of at least about 20 g/l.

[0064] It is a particular advantage of the oxalate formation step **194** of this embodiment that a substantial majority of the non-REE elements do not report with the REE-oxalate product **170**, *i.e.*, they remain solubilized in an REE-depleted solution **198**.

[0065] Exemplary compositions of pregnant liquor solutions are illustrated in **Table I**.

Table I

Element	PLS Example 1 (mg/l)	PLS Example 2 (mg/l)	PLS Exemplary Range (mg/l)
F	3610	3380	3000 – 4000
Al	4555	4593	4000 – 5000
Ba	2126	2147	2000 – 2500

Ca	3045	3151	3000-3200
Fe	22838	22733	22000 - 30000
K	1638	1653	1000-2000
Mg	1892	1995	1000-2000
Mn	13349	13514	10000-14000
Na	17733	--	10000 - 180000
P	70	71	60 - 80
Pb	1011	1058	1000-1200
S	<100	<100	10-80
Si	47	49	40-50
Th	40	70	40-70
Ti	296	309	250-350
U	40	34	30-60
Zn	1210	1297	1000-3000
REEs	35737	36369	> 35000

[0066] As can be seen from **Table I**, pregnant liquor solutions, e.g., from the leaching of a rare earth ore concentrate with HCl, may also contain appreciable amounts of non-REE elements, including base metals and other undesirable metals such as uranium and thorium. It is a significant advantage of this embodiment that REE-oxalates may be precipitated from the PLS, while a substantial majority of the non-REE elements remain in solution, *i.e.*, do not form oxalate compounds during the oxalate formation step. Particularly, very low concentrations of elements such as Al, Fe, Ca, Mg, Mn, P, Pb, S, Ti, U and/or Zn will precipitate with the REE-oxalates. As a result, the REE-oxalate product is of very high purity and a substantial proportion of the base metals and other metals such as uranium can be removed prior to extraction of the REEs, e.g., in a solvent extraction process.

[0067] The oxalate formation method of this embodiment to extract REEs includes contacting the PLS **190** with oxalic acid **192** in an oxalate formation step **194**, such as by contacting the reactants in a reactor **194** (e.g., a sealed reactor) under conditions such that REE-oxalate compounds (e.g., $RE_2(C_2O_4)_3$, $RE_3(C_2O_4)_3$, where RE = rare earth) precipitate from the PLS **190**. It will be appreciated that the REE-oxalate compounds may also be hydrated, e.g., $RE_2(C_2O_4)_3 \cdot xH_2O$. The PLS **190** is an acidic solution and may, for example, include free chloride ions. For example, the PLS **190**

may comprise hydrochloric acid (HCl) and may be obtained from the leaching of rare earth minerals (*e.g.*, a rare earth ore concentrate) with HCl. In one example, the PLS **190** has a free acid concentration (HCl) in the range of from about 0.5M to about 1M (*e.g.*, about 18.2 g/l to about 35.5 g/l HCl).

[0068] A sufficient amount of oxalic acid **192** is contacted with the PLS **190** in the reactor **202** to precipitate a majority of the REEs as REE-oxalates in an REE-oxalate product **170**. For example, the oxalic acid **192** (*e.g.*, fresh oxalic acid) input to reactor **202** may be an aqueous solution having a concentration of fresh oxalic acid in the range of at least about 38.4 g/l to about 52.5 g/l. Excess oxalic acid may be required and may be obtained by recycling various product streams in the process as is described herein.

[0069] Sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$) **210** may also be contacted with the PLS **190** in the oxalate formation step **194**, such as by adding the sodium oxalate **210** to the oxalic acid **192**, or by adding the sodium oxalate **210** directly to the PLS **190** in reactor **194**. As is illustrated in **Fig. 7**, the sodium oxalate **210** may advantageously be recycled from a subsequent process step, such as from crystallization step **236**, describe below. Alternatively, or in addition to, fresh sodium oxalate may be added to the oxalate formation step **194**. In one example, the ratio of (fresh) oxalic acid **192** to sodium oxalate **210** may be greater than 1, and in one particular characterization, the ratio of oxalic acid **192** to sodium oxalate **210** may be at least about 3:1 and not greater than about 4:1, such about 3.5:1. The addition of recycled sodium oxalate **210** to the oxalate formation step **194** may advantageously reduce the total consumption of oxalic acid by the process. This reduction in oxalic acid consumption may represent a significant cost savings for the process.

[0070] The oxalate formation step **194** may be carried out under reaction conditions such that the formation of REE-oxalates is favored over the formation of most non-REE oxalates from the PLS **190**. In one characterization, the oxalate formation step **194** is carried out by maintaining the reactants (*e.g.*, PLS **190**, oxalic acid **192** and optionally sodium oxalate **210**) at an elevated precipitation temperature (*e.g.*, a controlled precipitation temperature above ambient) of at least about 50°C and not greater than about 90°C, such as at least about 60°C or at least about 70°C, and not greater than

about 85°C. It has been found that a very high proportion of the REEs dissolved in the PLS **190** will precipitate as REE-oxalate particulates at such precipitation temperatures, while a comparatively low quantity of most non-REE elements (e.g., with the exception of thorium) will precipitate from the PLS **190**. Precipitation temperatures at the higher end of this range (e.g., from about 75°C to about 85°C) may result in higher purity metal oxalates, *i.e.*, a high content of REE-oxalates in the REE-oxalate product **170** and a relatively low content of non-REE oxalates in the REE-oxalate product **170**. In one characterization, the oxalate formation step **194** may be carried out by maintaining a precipitation temperature (e.g., in reactor **202**) for a sufficient amount of time to precipitate at least about 75 at.% of the REEs in the PLS **190** as particulate REE-oxalates such as, at least about 85 at.% of the REEs., at least about 90 at.% of the REEs, at least about 95 at.% of the REEs, or even at least about 98 at.%, at least about 99 at.% or 99.5 at.% of the REEs. In one example, the oxalate formation step **194** may be carried out for at least about 30 minutes and not greater than about 120 minutes, such as for about 60 minutes. The reactants may also be agitated (e.g., mixed) in the reactor **202** during the oxalate formation step **194**.

[0071] After formation of oxalate precipitates in the reactor **194**, the metal oxalate precipitates may be allowed to crystallize (e.g., to grow) over a period of time and the REE-oxalate product **170** may then be separated from an REE-depleted solution **212** in a separation step **208**. For example, the mixture **214** may be allowed to cool over a period of time to allow crystallization of the metal oxalates to form the REE-oxalate product **170**.

[0072] If the mixture **214** from the oxalate formation step **194** is allowed to cool, it may take a long period of time (e.g., several days) for the metal oxalate precipitates to completely crystallize so that the REE-oxalate product **170** may be readily separated from the REE-depleted solution **212**. Alternatively, the temperature of the reactants may be increased to a second crystallization temperature (e.g., greater than the first precipitation temperature) to enhance (e.g., to accelerate) crystallization and growth of the metal oxalate precipitates, particularly of the REE-oxalates. It has been found that because a majority of the initially available oxalate ion ($C_2O_4^{2-}$) is consumed in the

formation step **194** at the precipitation temperature, the increase in temperature in the crystallization step will not cause a substantial amount of non-REE elements to precipitate from the PLS **190**. The crystallization temperature is greater than the precipitation temperature, and in one characterization, the crystallization temperature is at least about 5°C greater than the precipitation temperature, such as at least about 7°C greater than the precipitation temperature. In another characterization, the crystallization temperature is at least about 90°C, such as at least about 92°C and is not greater than about 100°C, such as not greater than about 98°C. The crystallization of the oxalates may be carried out in the same reactor as the precipitation of the oxalates (e.g., in reactor **194**), or may be carried out in a separate reactor (not illustrated).

[0073] The crystallization temperature may be maintained for a time sufficient to grow the REE-oxalate particulates to a size that is suitable for subsequent separation **208** from the remaining REE-depleted solution **212**. In one characterization, the crystallization temperature is maintained for a period of time sufficient to grow the REE-oxalate precipitates to an average size (e.g., diameter) of at least about 50 nm, such as at least about 65 nm. In one particular characterization, the REE-oxalate precipitates are crystallized to an average size of from about 50 nm to about 85 nm. For example, the crystallization temperature may be maintained for at least about 4 hours and not greater than about 8 hours, such as for about 6 hours.

[0074] After crystallization, REE-oxalate product **170** may be separated from the REE-depleted solution **212** in a separation step **208**. For example, the separation step **208** may include the use of a micro-filter **216** to separate the REE-oxalate product **170** from the REE-depleted solution **212**.

[0075] The REE-oxalate product **170** comprises predominately REE-metal oxalates. It is an advantage of the oxalate formation step **194** that the REE-oxalate product **170** may be of high purity. For example, the total non-REE metals (e.g., Ba, Na, K, Si, Sr and/or Th) may constitute not greater than about 5 wt.% of the REE oxalate product **170**, such as not greater than about 3 wt.% or even not greater than 1 wt.%. **Table II** illustrates the elemental metal concentrations of exemplary REE-oxalate products, *i.e.*,

expressed as percentages of the total metal content, as determined by inductively coupled plasma (ICP) analysis.

Table II

Element	Ex. 1 Concentration (at.% of total metals)	Ex. 2 Concentration (at.% of total metals)
REEs	~98.2	~92.5
F	0.00	0.00
Al	<0.01	<0.01
Ba	0.44	1.00
Ca	0.16	<0.10
Fe	0.16	0.58
K	0.14	<1.00
Mg	<0.01	<0.01
Mn	<0.1	<0.1
Na	0.08	<0.1
P	0.04	0.24
Pb	0.04	<0.10
S	0.04	0.04
Si	0.02	<0.50
Th	0.52	0.58
Ti	0.02	<0.10
U	0.00	0.00
Zn	<0.01	<0.10
Total Non-REEs	~1.74	~7.04
Th + U	~0.52	~0.58

[0076] As is illustrated by **Table II**, the oxalate formation step **194** may advantageously selectively precipitate REE-oxalates from the PLS **190**, e.g., to the exclusion of non-REE elements such as base metals.

[0077] Thus, the REE-depleted solution **212** may be an acidic solution that includes solubilized metals that did not precipitate, *e.g.*, to form a metal oxalate, during the oxalate formation step **194**. For example, the REE-depleted solution **212** may include solubilized elements as listed in **Table II** such as Fe, Mn, Th, U, F, Al, Ca, K, Mg, Na, Sr, Zn, P, S, Pb and Ti. In one characterization, the REE-depleted solution **212** includes not greater than about 0.5 g/l REEs, such as no greater than about 0.25 g/l REEs. In another characterization, the REE-depleted solution **212** contains no greater than about 10 ppm thorium, such as from about 1 ppm to 10 ppm thorium. The REE-depleted solution **212** may have high free acid content, and the free acid content may be higher than the free acid content of the PLS **190**. For example, the free acid content (HCl) of the REE-depleted solution **212** may be greater than about 100 g/l, such as greater than about 110 g/l. In another characterization, the free acid content of the REE-depleted solution **212** may be at least about 1.5 times greater than the free acid content of the PLS **190**, such as at least about 2 times greater.

[0078] As is describe above, the REE-oxalate product **170** may include a high concentration of the REEs in the form of REE-oxalates. In one characterization, at least about 95% of the total metallic elements in the REE-oxalate product **170** are REEs, such as at least about 97% and even at least about 99% of the total metallic elements. Any remaining non-REE metal oxalates (*i.e.*, impurities) may comprise, for example, oxalates of Ba, Na, K, Si and Th. Stated another way, based on the total metals content of the REE-oxalate product **170**, the product **170** may include no greater than about 5 at. % non-REE metals, such as no greater than about 3 at. % non-REE metals and even no greater than about 1 at % non-REE metals.

[0079] The REE-depleted solution **212** may be recycled to conserve acid (*e.g.*, HCl acid), which may be particularly advantageous due to the relatively high free acid content of the REE-depleted solution **212**. For example, as illustrated in **Fig. 7**, the REE-depleted solution **212** may be transferred to a thickening step **218** such as in a thickener **220**. After thickening **218**, a separation step **222** may be carried out to separate oxalates **224**, which then may be recycled to the oxalate formation step **194**, from an acidic solution **226**, *e.g.*, an acidic solution that includes a high concentration of

chloride ions. The solution **226** may be subjected to a distillation step **228** using a distiller **230** to recover water **232**, which may be used as process water in other process steps, and acid **238**, which may also be recycled to other process steps such as a leaching step described below. Residue **234** may be further treated in a crystallization step **236** to recover and recycle oxalic acid crystals **242** and a by-product **244** that contains metals. The by-product **244** may be processed to recover further metals of value, such as gold, uranium, aluminum, manganese, iron, magnesium, strontium and zinc. The residue may be transferred to a crystallization step **236**, where oxalic acid crystals **176** may be recovered and recycled.

[0080] As is noted above, the PLS **190** may be derived from the leaching of rare earth mineral ore, such as an ore concentrate. **Fig. 8** illustrates a schematic flowsheet for one such leaching process. It will be appreciated that the leaching process illustrated in **Fig. 8** is only exemplary, and that other leaching processes for forming a pregnant liquor solution may also be employed in accordance with this disclosure.

[0081] As illustrated in **Fig. 8**, the leaching process may include leaching a rare-earth ore concentrate **246** with an acid **248** such as HCl acid in a counter-current flow to enhance leaching efficiency and reduce acid consumption. As is known to those skilled in the art, the ore concentrate **246** may be derived from rare earth containing minerals such as bastnaesite, monazite, carbonatite, loparite, or similar rare earth containing minerals. After separation from waste rock and other debris, the rare earth minerals may be beneficiated (e.g., milled) to reduce particle size and increase surface area of the minerals, and subjected to further separation such as by flotation and/or magnetic separation. A typical rare earth ore concentrate will include about 30% to about 70% rare earth oxides.

[0082] To extract metal values from the rare earth ore concentrate **246**, the concentrate **246** may be first contacted with recycled PLS **250** (e.g., containing HCl) in a pre-leaching step **252**. In addition to the ore concentrate **246** and the recycled PLS **250**, the pre-leaching step **252** may optionally include the addition of a reducing compound **254**, for example a sulfur-containing compound such as sodium sulfite (Na_2SO_3). The addition of a sulfur-containing compound such as sodium sulfite may

advantageously precipitate barium (Ba) and radium (Ra) as their sulfates from the PLS **246**. Further, the sulfur may reduce iron (Fe) in the PLS **246**. Specifically, the compound **254** may be selected to reduce at least a portion of the Fe in the PLS **246** from a +3 oxidation state to a +2 oxidation state. As is described herein, the leaching process may be integrated with a step that includes precipitating REE-oxalates from the PLS **246** by the addition of oxalic acid. However, Fe^{3+} may disadvantageously consume oxalic acid, and may increase the reagent costs for the overall process. By reducing the Fe^{3+} concentration in the PLS **246** and maintaining a substantial majority of the iron in the Fe^{2+} state, downstream consumption of oxalic acid may be reduced.

[0083] The pre-leaching step **252** is advantageously integrated (*e.g.*, in counter-current flow) with a primary leaching step **256**. In the primary leaching step **256**, pre-leached ore concentrate **246a** is contacted with additional acid **248** (*e.g.*, HCl) to leach metals from the pre-leached ore concentrate **246a**. For example, the primary leaching step **256** may include contacting the pre-leached ore concentrate **246a** with fresh HCl **248** and/or recycled HCl **238**, *e.g.*, recycled PLS from distillation **228** (**Fig. 7**). A reducing compound **254** may also be used in the primary leaching step **256**, as is described above with respect to pre-leaching step **252**. The primary leaching step **256** may be carried out at an elevated temperature, such as at least about 40°C to not greater than about 95°C, for a period of time and under conditions (*e.g.*, agitation) sufficient to solubilize substantially all of the REEs (*e.g.*, at least about 95 wt. % of the REEs) in the pre-leached ore concentrate **246a**. In one particular example, the primary leaching step is carried out of a temperature of from about 50°C to about 70°C to reduce dissolution of barium. The use of lower leaching temperatures (*e.g.*, 50°C) may also reduce the capital expense of the reactor by enabling fiberglass reactors to be utilized. In one characterization, the primary leaching step **256** is carried out for about 6 hours (*e.g.*, for an average residence time of about 6 hours).

[0084] After primary leaching **256**, a solid/liquid separation step **258** may be carried out to separate an acidic solution **250** comprising REEs from leach solids **260**, which then may be treated (*e.g.*, with hydroxides or carbonates) to neutralize the leach solids before disposal as tailings. The acidic solution **250** may be conveyed to the pre-leach

step **252**, after which the final PLS **190** is separated from the pre-leached ore concentrate **246a** in a separation step **262**, *e.g.*, in a substantially continuous process.

[0085] The RE ore concentrate **246** will typically include other elements in addition to the REEs, including metallic elements and non-metallic elements. **Table I** above illustrates the predominant elements that may be found in an exemplary pregnant liquor solution (PLS) extracted from the acidic leaching of an RE ore concentrate.

[0086] As is discussed above, it is an advantage of the methods disclosed herein that the final REE product is of very high purity, and includes low concentrations of non-REE elements such as base metals, uranium and thorium. Such a high purity REE product may be produced by combining the oxalate formation step described above with a metathesis step to convert the REE-oxalates to REE-carbonates, digesting the REE-carbonates in an acid and selectively precipitating thorium as thorium hydroxide from the solubilized REEs

[0087] Comprehensive flowsheets incorporating various embodiments of the foregoing methods are illustrated in **Figs. 9A and 9B**. In accordance with these flowsheets, a rare earth ore concentrate is leached in hydrochloric acid to form a pregnant liquor solution. Rare earth metals in the form of REE-oxalates are then precipitated from the pregnant liquor solution, and the REE-oxalates are then converted to REE-carbonates in a metathesis reaction. The REE-carbonate product, which also includes thorium carbonate, is then digested in nitric acid and the thorium is precipitated as thorium hydroxide by the addition of a hydroxide precipitant, leaving a nitrate solution that is rich in REEs and contains a very low concentration of other metals, including thorium, uranium and base metals. This nitrate solution can then be treated in a solvent extraction circuit to extract high purity rare earth metals (**Fig. 9A**), or can be treated to form REE-oxides (**Fig. 9B**).

[0088] Referring to both **Fig. 9A** and **Fig. 9B**, a rare earth ore concentrate **246** is subjected to a leaching circuit to form a PLS **190** substantially as described with respect to **Fig. 8**. The leaching process may include leaching a rare-earth ore concentrate **246** with an acid **248** such as HCl acid in a counter-current flow to enhance leaching efficiency and reduce acid consumption.

[0089] The concentrate **246** may be first contacted with recycled PLS **250** (*e.g.*, containing HCl) in a pre-leaching step **252**. In addition to the ore concentrate **246** and the recycled PLS **250**, the pre-leaching step **252** may optionally include the addition of a reducing compound **254**, for example a sulfur-containing compound such as sodium sulfite (Na_2SO_3) to precipitate barium (Ba) and/or radium (Ra), and/or to reduce Fe^{3+} to Fe^{2+} in the PLS **246**. The pre-leaching step **252** is advantageously integrated (*e.g.*, in counter-current flow) with a primary leaching step **256**. As illustrated in **Figs. 9A and 9B**, recycled HCl **238**, *e.g.*, recycled PLS from a subsequent distillation step **228** may be contacted with the incoming ore concentrate **246**. In the primary leaching step **256**, pre-leached ore concentrate **246a** is contacted with additional acid **248** (*e.g.*, HCl) to leach metals from the pre-leached ore concentrate **246a**. A reducing compound **254** may also be used in the primary leaching step **256**, as is described above with respect to pre-leaching step **252**. The primary leaching step **256** may be carried out at an elevated temperature, such as at least about 40°C to not greater than about 95°C, for a period of time and under conditions (*e.g.*, agitation) sufficient to solubilize substantially all of the REEs (*e.g.*, at least about 95 wt. % of the REEs) in the pre-leached ore concentrate **246a**. In one particular example, the primary leaching step is carried out at a temperature of from about 50°C to about 70°C to reduce dissolution of barium. The use of lower leaching temperatures (*e.g.*, about 50°C) may also reduce the capital expense of the reactor by enabling fiberglass reactors to be utilized. In one characterization, the primary leaching step **256** is carried out for about 6 hours (*e.g.*, for an average residence time of about 6 hours).

[0090] After primary leaching **256**, a solid/liquid separation step **258** may be carried out to separate an acidic solution **250** comprising REEs from leach solids **260**. The leach solids may be treated (*e.g.*, with hydroxides or carbonates) to neutralize the leach solids **260** before disposal as tailings. The acidic solution **250** may be conveyed to the pre-leach step **252**, after which the final PLS **190** is separated from the pre-leached ore concentrate **246a** in a separation step **262**, *e.g.*, in a substantially continuous leaching circuit.

[0091] In addition to REEs, the PLS **190** may also include non-REE elements that are solubilized in the PLS **190**, as is discussed above. It is a significant advantage of this embodiment that REE-oxalates may be precipitated from the PLS **190**, while a substantial majority of the non-REE elements remain in solution, *i.e.*, do not form oxalate compounds during the oxalate formation step. Particularly, very low concentrations of elements such as Al, Fe, Ca, Mg, n. P, Pb, S, Ti, U and/or Zn will precipitate with the REE-oxalates. As a result, the REE-oxalate product is of very high purity and a substantial proportion of the base metals and other metals such as uranium can be removed prior to extraction of the REEs, *e.g.*, in a solvent extraction process.

[0092] After formation of the PLS **190**, the PLS **190** is subjected to an oxalate formation step **194** where REEs and thorium are precipitated from the PLS **190**, while a large proportion of other metals (*e.g.*, base metals and uranium) advantageously remain in solution. The oxalate formation step **190** includes contacting the PLS **190** with oxalic acid **192** under conditions such that REE-oxalate compounds precipitate from the PLS **190**. A sufficient amount of oxalic acid **192** is contacted with the PLS **190** to precipitate a majority of the REEs as REE-oxalates in an REE-oxalate product **170**. Sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$) **210** may also be contacted with the PLS **190** in the oxalate formation step **194**, such as by adding the sodium oxalate **210** to the oxalic acid **192**, or by adding the sodium oxalate **210** directly to the PLS **190**. As is illustrated in **Figs. 9A** and **9B**, recycled sodium oxalate **224** may advantageously be input to the oxalate formation step **194** from a subsequent process step, such as from a thickening step **218** and separation step **222**. Alternatively, or in addition to, fresh sodium oxalate **210** may be added to the oxalate formation step **194**. In one example, the ratio of (fresh) oxalic acid **192** to sodium oxalate **210** may be greater than 1, and in one particular characterization, the ratio of oxalic acid **192** to sodium oxalate **210** may be at least about 3:1 and not greater than about 4:1, such about 3.5:1. As is noted above, the addition of recycled sodium oxalate **224** to the oxalate formation step **194** may advantageously reduce the total consumption of oxalic acid by the process, *i.e.*, by the oxalate formation step **194**. This reduction in oxalic acid consumption may represent a significant cost savings for the process.

[0093] As is described above with respect to **Fig. 7**, the oxalate formation step **194** may be carried out under conditions such that the formation of REE-oxalates is favored over the formation of most non-REE oxalates from the PLS **190**. In one characterization, the oxalate formation step **194** may be carried out by maintaining a precipitation temperature for a sufficient amount of time to precipitate at least about 75 at.% of the REEs in the PLS **190** as particulate REE-oxalates such as, at least about 85 at.% of the REEs., at least about 90 at.% of the REEs, at least about 95 at.% of the REEs, or even at least about 98 at.%, at least about 99 at.% or 99.5 at.% of the REEs. In one example, the oxalate formation step **194** may be carried out for at least about 30 minutes and not greater than about 120 minutes, such as for about 60 minutes.

[0094] After formation of oxalate precipitates, the metal oxalate precipitates may be allowed to crystallize (e.g., to grow) over a period of time and the REE-oxalate product **170** may then be separated from an REE-depleted solution **212** in a separation step **208**. For example, the mixture **214** may be allowed to cool over a period of time to allow crystallization of the metal oxalates to form the REE-oxalate product **170**. Alternatively, the temperature of the reactants may be increased to a second crystallization temperature (e.g., greater than the first precipitation temperature) to enhance (e.g., to accelerate) crystallization and growth of the metal oxalate precipitates, particularly of the REE-oxalates. The crystallization of the oxalates may be carried out in the same reactor as the precipitation of the oxalates, or may be carried out in a separate reactor.

[0095] After crystallization, REE-oxalate product **170** may be separated from the REE-depleted solution **212** in a separation step **208**. The REE-oxalate product **170** comprises predominately REE-metal oxalates and the REE-oxalate product **170** may be of very high purity. For example, the total non-REE metals (e.g., Ba, Na, K, Si, Sr and/or Th) may constitute not greater than about 5 wt.% of the REE oxalate product **170**, such as not greater than about 3 wt.% or even not greater than 1 wt.%.

[0096] The REE-depleted solution **212** may be an acidic solution that includes solubilized metals that did not precipitate, e.g., to form a metal oxalate, during the oxalate formation step **194**. For example, the REE-depleted solution **212** may include

solubilized elements as listed in **Table II** above such as Fe, Mn, Th, U, F, Al, Ca, K, Mg, Na, Sr, Zn, P, S, Pb and Ti. The REE-depleted solution **212** may have high free acid content, and the free acid content may be higher than the free acid content of the PLS **190**. As a result, the REE-depleted solution **212** may be recycled to conserve acid (e.g., HCl acid). As illustrated in **Figs. 9A** and **9B**, the REE-depleted solution **212** may be transferred to a thickening step **218**. After thickening **218**, a separation step **222** may be carried out to separate oxalates **224** (e.g., sodium oxalates), which then may be recycled to the oxalate formation step **194**. The acidic solution **226** will contain a high concentration of chloride ions, and the solution **226** may be subjected to a distillation step **228** to recover water **232** and an acid **238**. The water may be used as process water in other process steps, such as in a subsequent metathesis step **172**, for filter washing etc. The **238** may also be recycled to other process steps such as a leaching step **252** and/or **256**. As illustrated in **Figs. 9A** and **9B**, the acid is recycled to the pre-leaching step **252** in a closed loop. Residue **234** from the distillation may be further treated in a crystallization step **236** to recover and recycle additional oxalic acid crystals **242** to the oxalate formation step **194**, further reducing the consumption of oxalic acid by the process. The by-product **244** from the crystallization step **236** contains metals, and may be processed to recover further metals of value, such as gold, uranium, aluminum, manganese, iron, magnesium, strontium and zinc.

[0097] The foregoing process steps described with respect to **Figs. 9A** and **9B** illustrate various ways that reagents (e.g., hydrochloric acid and oxalic acid) may be recycled within the process to significantly reduce reagent consumption and reduce operating expenses associated with the process.

[0098] As is described above with respect to **Figs. 5** and **6**, the high purity REE-oxalate product **170** is converted in a metathesis step **172** to a REE-carbonate product **174** for subsequent dissolution of the REE-carbonate product **174** in an acid, e.g., to solubilize the REEs and thorium in an acid digestion step **122**. In this embodiment, an REE-oxalate product **170** is contacted with a carbonate compound **176** such as sodium carbonate (Na_2CO_3) in the metathesis step **172**, along with a solvent such as water (e.g., recycled water **232**), which may be introduced with the other reactants or may be

introduced separately. The only by-product of the metathesis step **172** is a high-purity carbon dioxide stream **182** which may be captured as a by-product.

[0099] In a separation step **184**, the REE-carbonate product **174** (e.g., REE-carbonate particulates) may be separated from an oxalate solution **186** such as by using a filter **188**. The oxalate solution **186** will include substantial amounts of dissolved oxalates (e.g., $\text{Na}_2\text{C}_2\text{O}_4 \cdot y\text{H}_2\text{O}$ when the carbonate compound **176** is sodium carbonate) and the oxalate solution **186** may advantageously be recycled back to the oxalate formation step **194** to further reduce the consumption of fresh reagents.

[00100] After formation of the high purity REE-carbonate product **174**, the product **174** may be contacted with nitric acid **120** (e.g., fresh nitric acid or sulfuric acid) in an acid digestion step **122**. The resulting acidic solution **102** may be an acidic solution substantially as described above with respect to **Figs. 1** and **2** above. The acidic solution **102** may then be contacted in a first hydroxylation step **110a** with a hydroxide precipitant **104a** to precipitate a thorium hydroxide product **108a** from the acidic solution **102**. The thorium hydroxide product **108a** may be separated from the thorium depleted solution **106b** in a separation step **114a**. Thereafter, the intermediate thorium depleted solution **106b** may be contacted in a second hydroxylation step **110b** with a second hydroxide precipitant **104b** to form the thorium depleted solution **106**. The thorium depleted solution **106** may then be separated from the second thorium hydroxide product **108b** in a separation step **114b**.

[00101] The amount of thorium hydroxide product **108b** may be relatively small and there may be appreciable quantities of REEs in the thorium hydroxide product **108b**. To reduce losses of REEs, the thorium hydroxide product **108b** may advantageously be recycled back to the acid digestion step **122** where the thorium is re-digested with the REE-carbonate product **174**. In this manner, all of the thorium hydroxide is removed from the acidic solution **102** with the first thorium hydroxide product **108a**. When the thorium hydroxide product **108b** is separated in separating step **114b**, the resulting thorium depleted solution **106** is a relatively high purity REE-nitrate solution (or REE-sulfate solution in the event sulfuric acid is utilized in the digestion step **122**).

[00102] Referring now to Fig. 9A, the high purity REE-nitrate solution **106** may then be subjected to a solvent extraction circuit **126** to extract REEs as metals from the thorium depleted solution **106**. Having the REEs solubilized in nitrate media (nitric acid) may reduce the expenses associated with a solvent extraction circuit **126**. The solvent extraction circuit **126** may include the steps of solvent extraction **128** and solvent stripping **130** with a stripping solvent **132**. Because the thorium depleted solution **106** described herein is of extremely high purity, the solvent extraction circuit **126** may advantageously be operated at a reduced capital expense and reduced operating expense. The resulting products are very high purity and high value REE metals **134**.

[00103] The thorium depleted solution **106** may also include substantial quantities of highly salable ammonium nitrate. Thus, an ammonium nitrate removal step **136** may be utilized to continuously or intermittently remove ammonium nitrate **138** from the solution **106**. As illustrated in **Fig. 9A**, the ammonium nitrate is removed after the solvent extraction circuit **126**, as the presence of ammonium nitrate in the thorium depleted solution **106** is not believed to impair the efficacy of the solvent extraction circuit **126**. However, it will be appreciated that the ammonium nitrate separation step may also occur before the solvent extraction circuit **126** if desired.

[00104] The ammonium nitrate separation step **136** may include cooling the REE-depleted acidic solution **148** to a reduced temperature (*e.g.*, below about 10°C) to crystallize ammonium nitrate **138**. Because ammonium nitrate **138** is highly soluble in acid, it may only be necessary to intermittently operate the separation step **136** to remove ammonium nitrate **138**. Ammonium nitrate is valuable and salable by-product that is widely used in the fertilizer industry and may represent a significant source of revenue from the process. After separation of the ammonium nitrate **138** (intermittently or continuously), the resulting acid **140** (*e.g.*, recycled nitric acid) may be recycled back to the process, *e.g.*, back to the acid digestion step **122**. Thus, the acid (*e.g.*, input at **120**) may be contained in an essentially "closed loop" within the process. Additional acid may be generated during the solvent extraction circuit due to cationic ion exchange releasing protons into solution. In this regard, a substantial quantity of the acid required for the acid digestion step may be provided by the recycled acid **140**, and only a small

amount of fresh acid **120** may be required for the process once steady state and continuous operations are achieved and maintained.

[00105] Referring now to **Fig. 9B**, an REE precipitation circuit replaces the solvent extraction circuit of **Fig. 9A**. Thus, the thorium depleted and REE-nitrate rich solution can be treated to precipitate high purity REE-compounds such as REE-oxides and/or REE-hydroxides which, for example, may be shipped to a separate facility for extraction of the REEs as metals. See **Fig. 4** described above.

[00106] The thorium depleted solution **106** from the separation step **114b** will typically have a pH in the range of about pH 3.6 to about pH 4 (e.g., about pH 3.8) and will be rich in REE-nitrates and may contain no, or extremely low levels of, thorium and/or uranium. This solution **106** is conveyed to an REE precipitation step **142**, where the solution **106** is contacted with an REE precipitation agent **144**, such as ammonium hydroxide, in sufficient quantities to increase the pH of the solution, such as by increasing the pH to at least about pH 4.5, such as at least about pH 4.9. In one characterization, the pH during the precipitation step **144** is not greater than about pH 6 and may be about pH 5.5. At these pH levels, the REEs will precipitate from the solution **106** as REE-hydroxides **146**, which may be separated from an REE-depleted nitrate solution **148** in a separation step **150**.

[00107] The REE-hydroxides **146** may then be converted from the REE-hydroxides to REE-oxides. The REE-hydroxides **146** are conveyed to a drying step **152** where the REE-hydroxides are heated to a drying temperature that is sufficient to convert a substantial majority of the REE-hydroxides **146** to REE-oxides **154**. In one example, the REE-hydroxides **146** are conveyed to a screw feed dryer for the substantially continuous production of the REE-oxides **154**. In another example, the REE-hydroxides **146** may be stockpiled as necessary and dried batchwise.

[00108] It is an advantage of this embodiment that the resulting REE-oxide product **154** will have a very high purity, particularly with respect to base metals and radioactive metals such as uranium and thorium. In one example, the REE-oxide product **154** has a purity of at least about 98%, *i.e.*, the REE-oxide product **154** comprises at least about

98% REE-oxides. Further, the REE-oxide product **154** may have a purity of at least about 99%, such as at least about 99.5%.

[00109] An REE-depleted nitrate solution **148** may also be recovered from the separation step **150**, and may have a high content of ammonium nitrate, such as from about 30 g/l to about 50 g/l ammonium nitrate. The solution **148** may be conveyed to a vessel **156** where ammonium hydroxide is stored for use in the process, *i.e.*, where the recycled nitrate solution **148** is added to fresh ammonium hydroxide **158**. An ammonium hydroxide product **160** such as an ammonium hydroxide solution may then be conveyed as needed to the process, *e.g.*, to hydroxylation steps **110a/110b** and/or to REE precipitation step **142**. Because the recycled REE-depleted nitrate solution will contain ammonium nitrates, it may be desirable to remove the ammonium nitrates from the ammonium hydroxide vessel **156** on a continuous or intermittent basis. In this regard, a portion **162** of the solution contained within vessel **156** may be periodically bled off from the vessel **156** and subjected to an ammonium nitrate precipitation step **164** to crystallize an ammonium nitrate by-product **166** and recycle an ammonium nitrate depleted solution **168** back to the vessel **156**. The ammonium nitrate by-product **166** will be of high purity and a valuable by-product of the process.

[00110] The flowsheets illustrated in **Figs. 9A and 9B** may provide at least one or more of the following advantages.

[00111] The metathesis step produces a REE-carbonate product that is soluble in relatively dilute concentrations of acid, *e.g.*, 6 wt.% or lower, as compared to other REE compounds such as REE-oxalates and REE-oxides. This results in a lower overall acid consumption and therefore reduced operating expense.

[00112] The metathesis advantageously removes uranium from the product, as uranium carbonate does not form during metathesis. In one example, at least about 95%, such as at least about 97% of the uranium contained in the pregnant liquor solution will be rejected during the metathesis step, leaving less than 5%, such as less than 3% of the initial uranium in the REE-carbonate product.

[00113] The metathesis step advantageously enables the oxalate reagents to be recycled back to the oxalate formation step, thereby reducing the consumption of fresh oxalic acid.

[00114] The resulting REE-nitrate solution is of extremely high purity, and contains extremely low quantities of radioactive elements such as radium, thorium and/or uranium. Essentially all radium may be removed with sulfites during leaching of the ore concentrate and subsequent oxalate formation steps. The bulk of the uranium is rejected at the oxalate formation step, and most remaining uranium is rejected during the metathesis step. Thorium is removed as thorium hydroxide when precipitated with a hydroxide precipitant. The REE-nitrate solution also is substantially free of suspended solids, such as silicate particulates, thereby substantially reducing crud or mud formation in the solvent extraction.

[00115] The REE-nitrate solutions may also reduce the capital expenses associated with the solvent extraction circuit as compared to other solutions such as REE-chloride solutions. For example, chloride solutions typically require titanium coated vessels to carry out the extraction. The use of a nitrate solution may eliminate this requirement.

[00116] The process may utilize several recycle streams and therefore is cost effective with respect to the reagents.

EXAMPLES

[00117] A pregnant liquor solution containing REEs is contacted with oxalic acid to precipitate metal oxalates. The precipitation temperature is about 70°C. No sulfite was added to the PLS, and therefore Fe^{3+} was present. No recycle was performed. The concentration of oxalic acid is varied from 90 g/l to 115 g/l to 140 g/l to assess the effect of oxalic acid concentration on the purity of the precipitate product (*i.e.*, the metal oxalates). Results are shown in **Table III**.

Table III

Element	Oxalate @ 90 g/l $\text{H}_2\text{C}_2\text{O}_4$ (wt.%)	Oxalate @ 115 g/l $\text{H}_2\text{C}_2\text{O}_4$ (wt.%)	Oxalate @ 140 g/l $\text{H}_2\text{C}_2\text{O}_4$ (wt.%)
REEs¹			
Ce	16.511467	16.61625	16.36584
La	8.549287	8.323717	7.840823
Nd	5.490483	5.67714	5.908091
Pr	1.594311	1.635.82	1.66676
Y	0.075021	0.075069	0.7525
TOTAL REEs	32.220569	30.6922	32.534
Impurity Elements			
Th		0.193692	0.218965
U	0.001687	0.001574	0.001865
Si	0.491763	0.46509	0.470356
Au	< LOD	< LOD	0.002628
As	0.002351	0.0011.58	0.002418
Se	< LOD	< LOD	< LOD
Pb	< LOD	< LOD	< LOD
Zn	< LOD	< LOD	< LOD
Cu	0.012393	0.012785	0.013937
Ni	0.032589	0.034371	0.03619
Co	0.071752	0.070868	0.070785
Fe	0.513656	0.530995	0.564361
Mn	< LOD	< LOD	< LOD
Cr	< LOD	< LOD	< LOD
V	< LOD	< LOD	< LOD
Ti	< LOD	< LOD	< LOD
Ca	< LOD	< LOD	< LOD
K	< LOD	< LOD	< LOD
Zr	< LOD	< LOD	< LOD
Mo	0.000372	0.000516	0.000781
Nb	0.000466	0.000678	<LOD
Sr	0.00376	<LOD	<LOD
Mn	< LOD	< LOD	< LOD
Cr	< LOD	< LOD	< LOD
V	< LOD	< LOD	< LOD
Ti	< LOD	< LOD	< LOD

Ca	< LOD	< LOD	< LOD
K	< LOD	< LOD	< LOD
Al	< LOD	< LOD	< LOD
Mg	< LOD	< LOD	< LOD
Zr	< LOD	< LOD	< LOD

1 – other REEs not analyzed

<LOD = below the limits of detection

[00118] As demonstrated by **Table IV**, REE-oxalates with a high proportion of REEs and a relatively low proportion of non-REEs can be obtained by oxalate precipitation over a range of oxalic acid concentrations, even at a precipitation temperature of about 70°C. In particular, it is noteworthy that many prior processes for separation of REEs from a pregnant liquor solution also precipitate many non-REE elements with the REEs, for example U, Si, As, Pb, Zn, Fe, Mn, Mo, Nb, Cr, Ti, Ca, K, Al and Zr.

[00119] In the following Example, thorium is precipitated from an acidic solution using a hydroxide precipitant at various pH levels to observe the effect of pH on the precipitation of thorium and of REEs.

[00120] For these tests, 400 grams (326 ml) of a nitric acid solution having a free acid content of about 5 g/l and a specific gravity of 1.227 is added to a one liter vessel having a mixer. A 1M solution of ammonium hydroxide (NH₄OH) is added dropwise to the vessel until the target pH level is reached, and the target pH is maintained for one hour. A temperature of about 25°C is maintained during the precipitation step. After 60 minutes, the vessel contents are filtered and the weight, specific gravity and free acid content of the filtrate are measured. The retentate is washed with deionized water and dried.

Table IV

Element	Acidic Solution Assay (mg/l or g/tonne)	% Precipitated @ pH 1.0	% Precipitated @ pH 2.0	% Precipitated @ pH 2.5	% Precipitated @ pH 3.0	% Precipitated @ pH 3.5
La	20000	7	5	4	0	2
Ce	13500	7	5	3	0	2

Pr	3150	3	0	7	0	19
Nd	11000	4	1	3	0	3
Sm	1580	4	0	8	0	19
Eu	352	3	0	7	0	19
Gd	814	2	0	5	0	15
Tb	62	3	0	8	4	22
Dy	204	2	0	5	0	17
Ho	24	2	0	4	1	19
Y	494	5	0	7	0	18
Er	40	3	0	7	0	15
Tm	4	4	4	3	0	18
Yb	19	7	6	5	2	21
Lu	3	5	5	5	2	21
Sc	<5	0	0	3	22	70
Th	734	4	1	8	62	95
U	1	0	0	0	0	24

[00121] The foregoing data is graphically illustrated in **Fig. 10A**. This data demonstrates that at pH 3.0, 62% of the thorium in the acidic solution may be precipitated as thorium hydroxide. When the pH is increased to pH 3.5, 95% of thorium is precipitated, however increasing amounts of REEs also begin to precipitate from the solution.

[00122] However, if thorium concentration in the solution is decreased, it is found that the pH can be increased without precipitating significant quantities of REEs from the solution. **Fig. 10B** illustrates the results of increasing the pH of a solution over a range

from pH 3.0 to pH 3.8, where the initial thorium concentration is decreased to 117 mg/l. As is illustrated in **Fig. 10B**, pH levels at least as high as pH 3.8 can be utilized to extract a high percentage of the thorium without precipitating significant amounts of the REEs. The results for the tests at pH 3.5, pH 3.6 and pH 3.8 for a solution containing 117 mg/l thorium are given in **Table V**.

Table V

Element	Feed Assay (mg/l or g/tonne)	Final Solution Assay @ pH 3.5 (mg/l or g/tonne)	Percent Removed @ pH 3.5	Final Solution Assay @ pH 3.6 (mg/l or g/tonne)	Percent Removed @ pH 3.6	Final Solution Assay @ pH 3.8 (mg/l or g/tonne)	Percent Removed @ pH 3.8
La	2710	2200	1	2220	0	2160	2
Ce	1870	1520	1	1540	0	1500	2
Pr	473	386	0	390	0	380	2
Nd	1630	1344	0	1364	0	1332	0
Sm	232	189	0	191	0	187	1
Eu	51.0	42	0	42	0	41	1
Gd	122	99	0	102	0	100	0
Tb	9.8	8	0	8	0	8	0
Dy	30.8	23	1	25	0	25	0
Ho	3.52	5	1	3	0	3	0
Y	74.4	60	1	61	0	59	3
Er	6.15	5.06	0	4.84	4	4.96	1
Tm	0.58	0.46	3	0.5	0	0.48	0
Yb	2.83	2.32	0	2.30	1	2.22	4
Lu	0.35	0.30	0	0.28	2	0.28	2

Sc	0.71	0.62	0	0.40	31	0.48	17
Th	117	69	28	65	32	51	46
U	0.22	0.18	0	0.18	0	0.18	0

[00123] As is illustrated in this Example, high levels of thorium can be extracted from a relatively dilute solution at increased pH levels, without extracting high levels of REEs from the solution.

[00124] While various embodiments have been described in detail, it is apparent that modifications and adaptations of those embodiments will occur to those skilled in the art. However, it is to be expressly understood that such modifications and adaptations are within the spirit and scope of the present disclosure.

What is Claimed is:

1. A method for the selective extraction of rare earth elements (REEs) from base metals in a pregnant liquor solution, comprising the steps of:

leaching a rare earth ore concentrate with HCl to form a pregnant liquor solution comprising at least chloride ions, solubilized rare earth elements and solubilized base metals, and comprising at least about 20 g/l iron;

contacting the pregnant liquor solution with oxalic acid, where the pregnant liquor solution has a strength of at least 0.5M HCl;

maintaining the pregnant liquor solution and the oxalic acid in contact at a first temperature to precipitate, from the pregnant liquor solution, a metal oxalate product comprising REE-oxalate particulates and form a REE-depleted solution; and

separating the metal oxalate product from the REE-depleted solution,

wherein the contacting step is conducted at the first temperature for a sufficient time such that at least 97% of the total metallic elements in the metal oxalate product are rare earth elements.

2. The method recited in Claim 1, further comprising the steps of:

recovering recyclable HCl from the REE-depleted solution; and

recycling the recyclable HCl to the leaching step.

3. The method recited in Claim 1, wherein the pregnant liquor solution comprises at least 20 g/l REEs.

4. The method recited in Claim 1, wherein the pregnant liquor solution comprises at least 30 g/l REEs.

5. The method recited in Claim 1, wherein the first temperature is at least 80°C.

6. The method recited in Claim 1, wherein the first temperature is not greater than 90°C.

7. The method recited in Claim 1, wherein the pregnant liquor solution and the oxalic acid are maintained in contact at the first temperature for a first period of time sufficient to precipitate at least 90 at.% of the REEs from the pregnant liquor solution as REE-oxalates.

8. The method recited in Claim 1, comprising the steps of:

after the maintaining at a first temperature, increasing the temperature of the mixture to a second temperature that is greater than the first temperature;
and

maintaining the mixture at the second temperature to crystallize the REE-oxalate particulates.

9. The method recited in Claim 8, wherein the second temperature is at least 5°C greater than the first temperature.

10. The method recited in Claim 8, wherein the second temperature is at least 90°C.

11. The method recited in Claim 8, wherein the second temperature is not greater than 98°C.

12. The method recited in Claim 1, wherein the contacting step comprises contacting the pregnant liquor solution with oxalic acid and sodium oxalate.

13. The method recited in Claim 1, wherein the pregnant liquor solution further comprises actinide elements.

14. The method recited in Claim 1, further comprising the step of:

subjecting the metal oxalate product to a metathesis step to convert the metal oxalates to metal carbonates.

15. A method for the selective extraction of rare earth elements from base metals in a pregnant liquor solution, comprising the steps of:

leaching a rare earth ore concentrate with HCl to form the pregnant liquor solution, the pregnant liquor solution comprising at least solubilized rare earth elements and solubilized base metals;

contacting the pregnant liquor solution with oxalic acid;

maintaining the pregnant liquor solution and the oxalic acid in contact at a first temperature of at least 80°C to precipitate a metal oxalate product comprising REE-oxalate particulates from the pregnant liquor solution and form a mixture of the metal oxalate particulates in a REE-depleted solution;

after the maintaining at a first temperature, increasing the temperature of the mixture to a second temperature that is at least 5°C greater than the first temperature;

maintaining the mixture at the second temperature to crystallize the REE-oxalate particulates; and

separating the metal oxalate product comprising the crystallized REE-oxalate particulates from the REE-depleted solution;

wherein at least 97% of the total metallic elements in the metal oxalate product are rare earth elements.

16. The method recited in Claim 15, wherein the pregnant liquor solution comprises at least 30 g/l REEs.

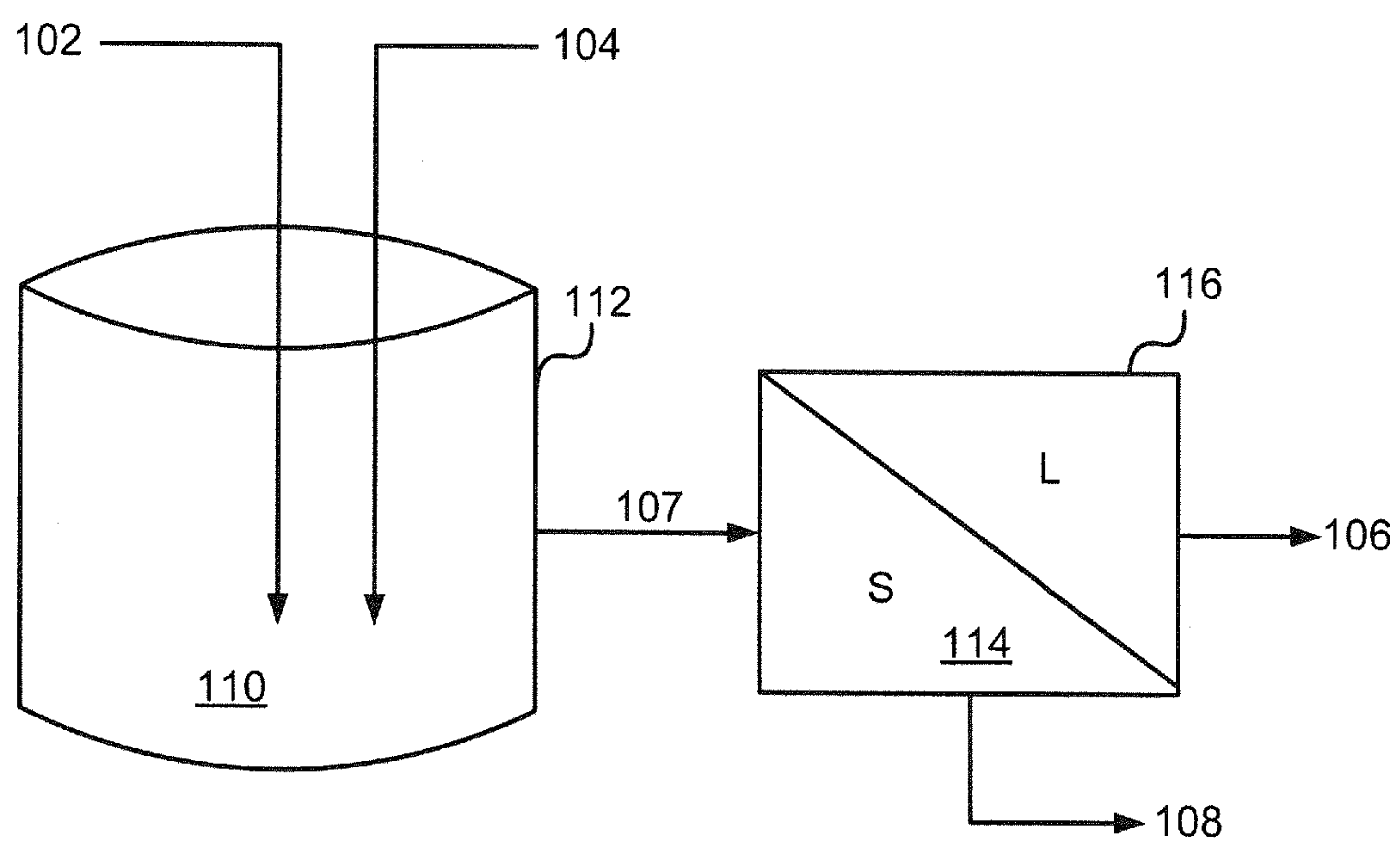
17. The method recited in Claim 15, wherein the pregnant liquor solution comprises at least 20 g/l iron.

18. The method recited in Claim 1, wherein the first temperature is at least 70°C.

19. The method recited in Claim 1, further comprising the step of:
recovering oxalate compounds from the REE-depleted solution after the separating step; and
recycling the oxalate compounds to the contacting step.

20. The method recited in Claim 1, wherein the free acid content of the REE-depleted solution after the separating step is higher than the free acid content of the pregnant liquor solution.

1/11

**FIG. 1**

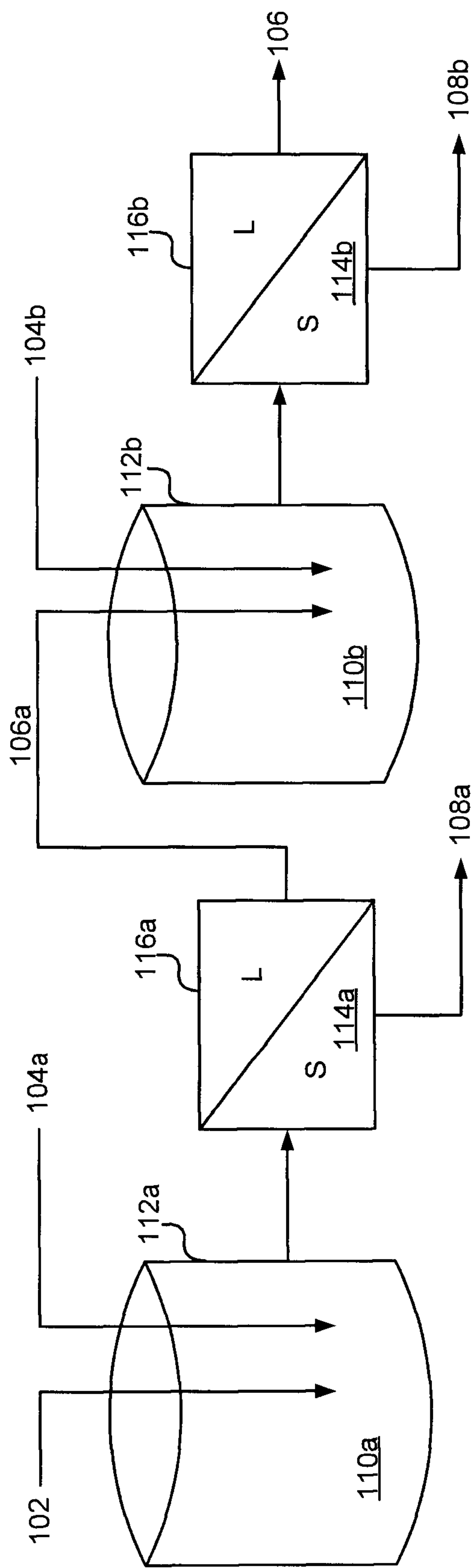


FIG. 2

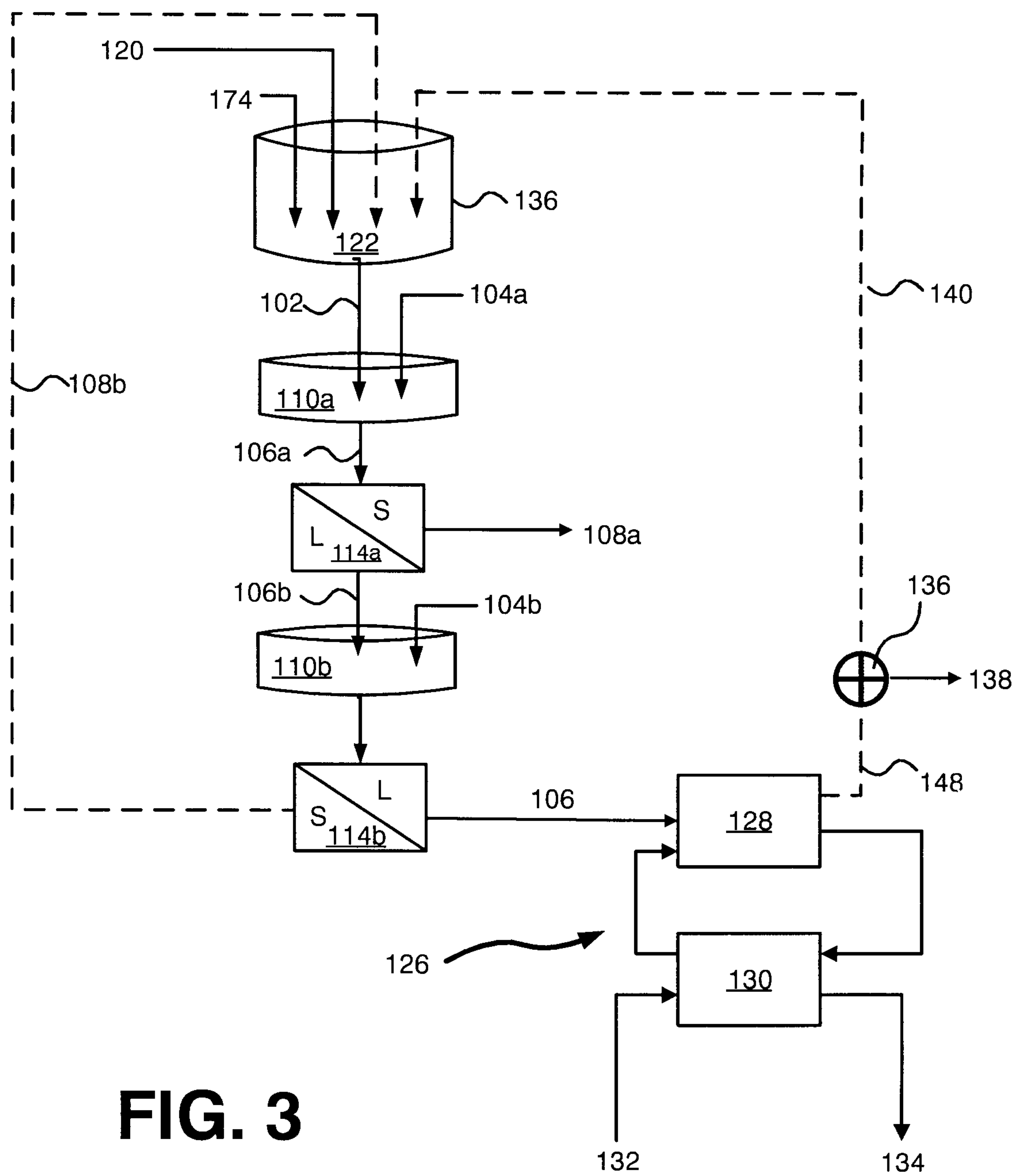
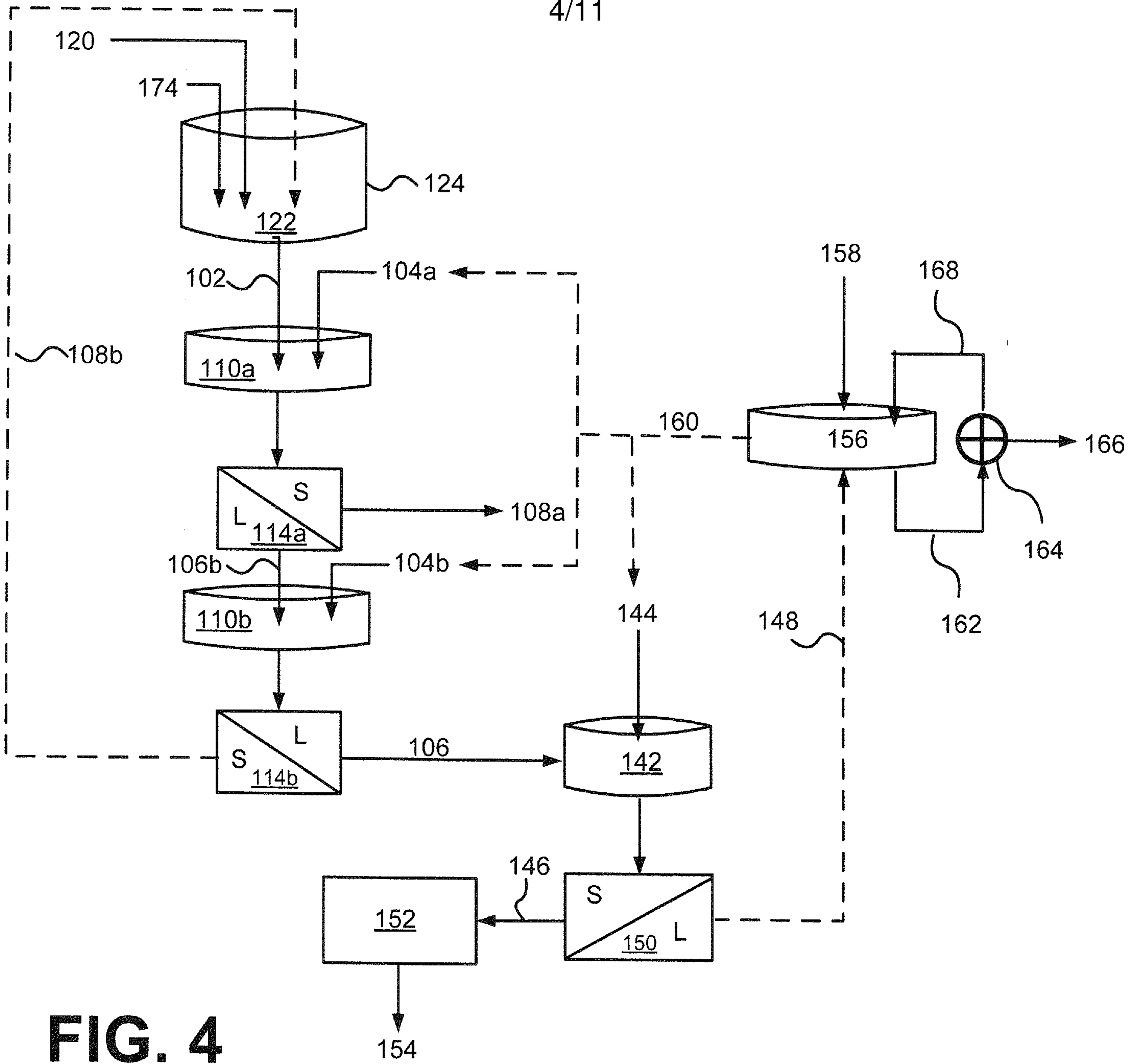


FIG. 3

4/11

**FIG. 4**

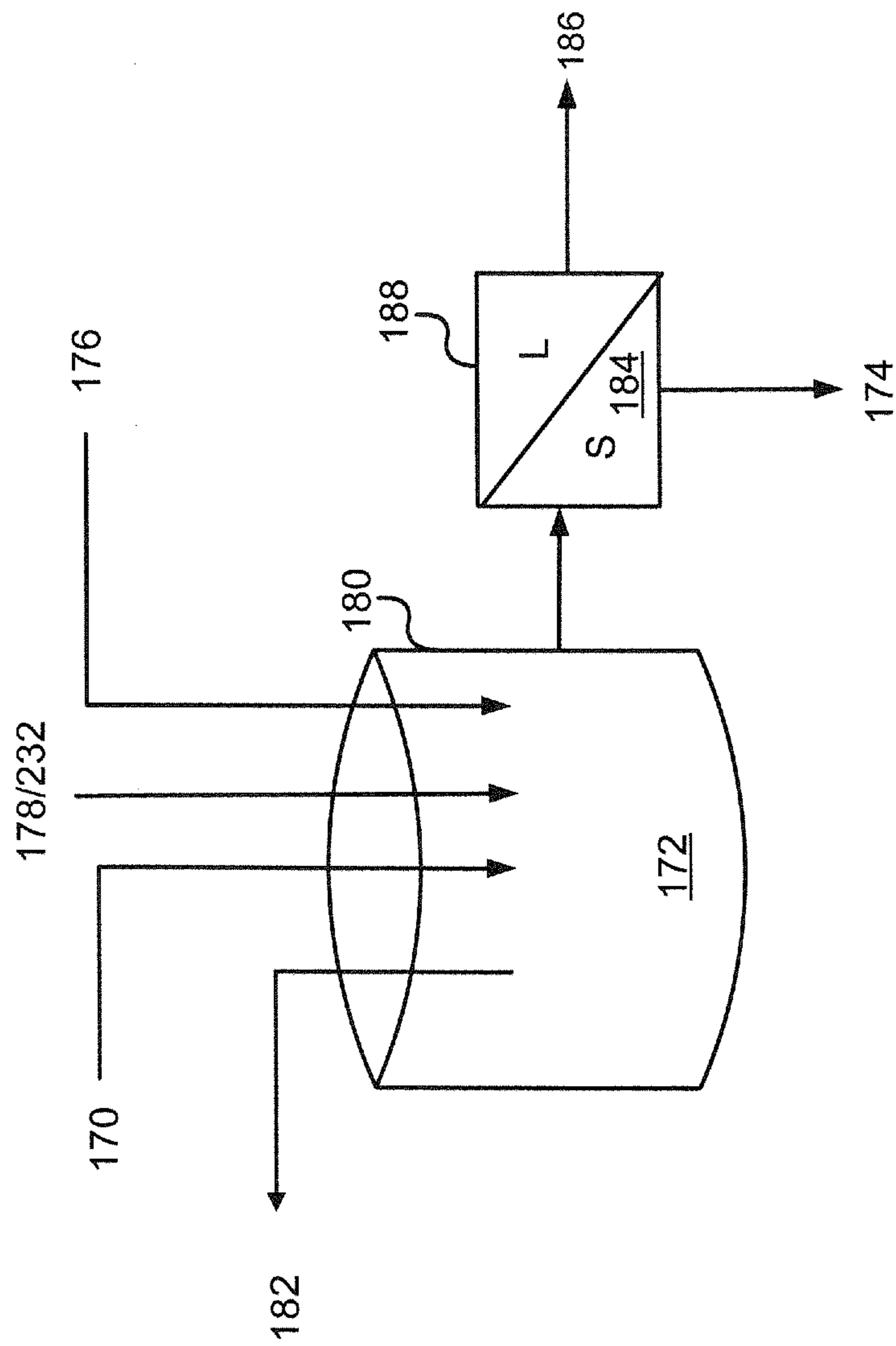
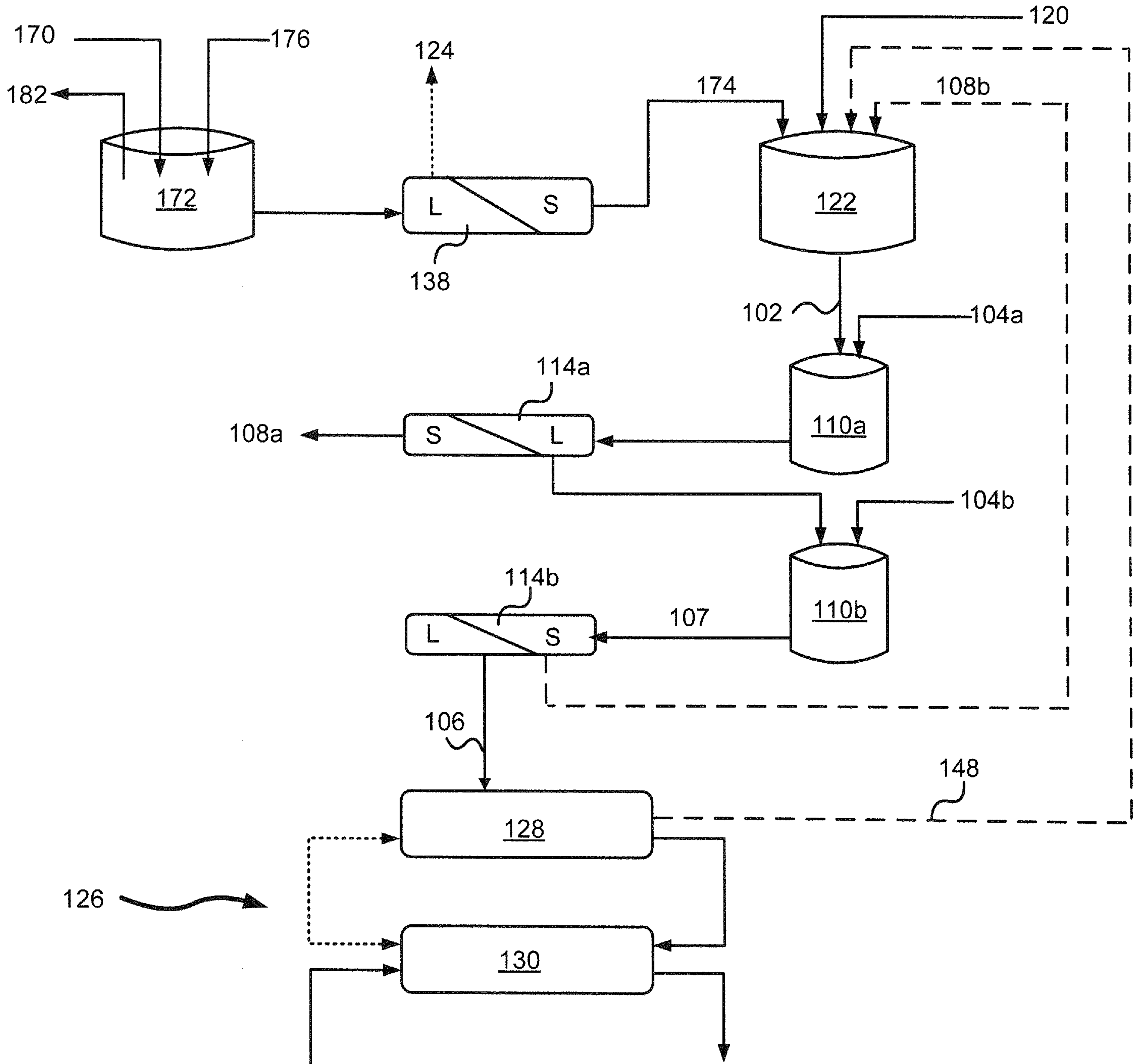


FIG. 5

**FIG. 6**

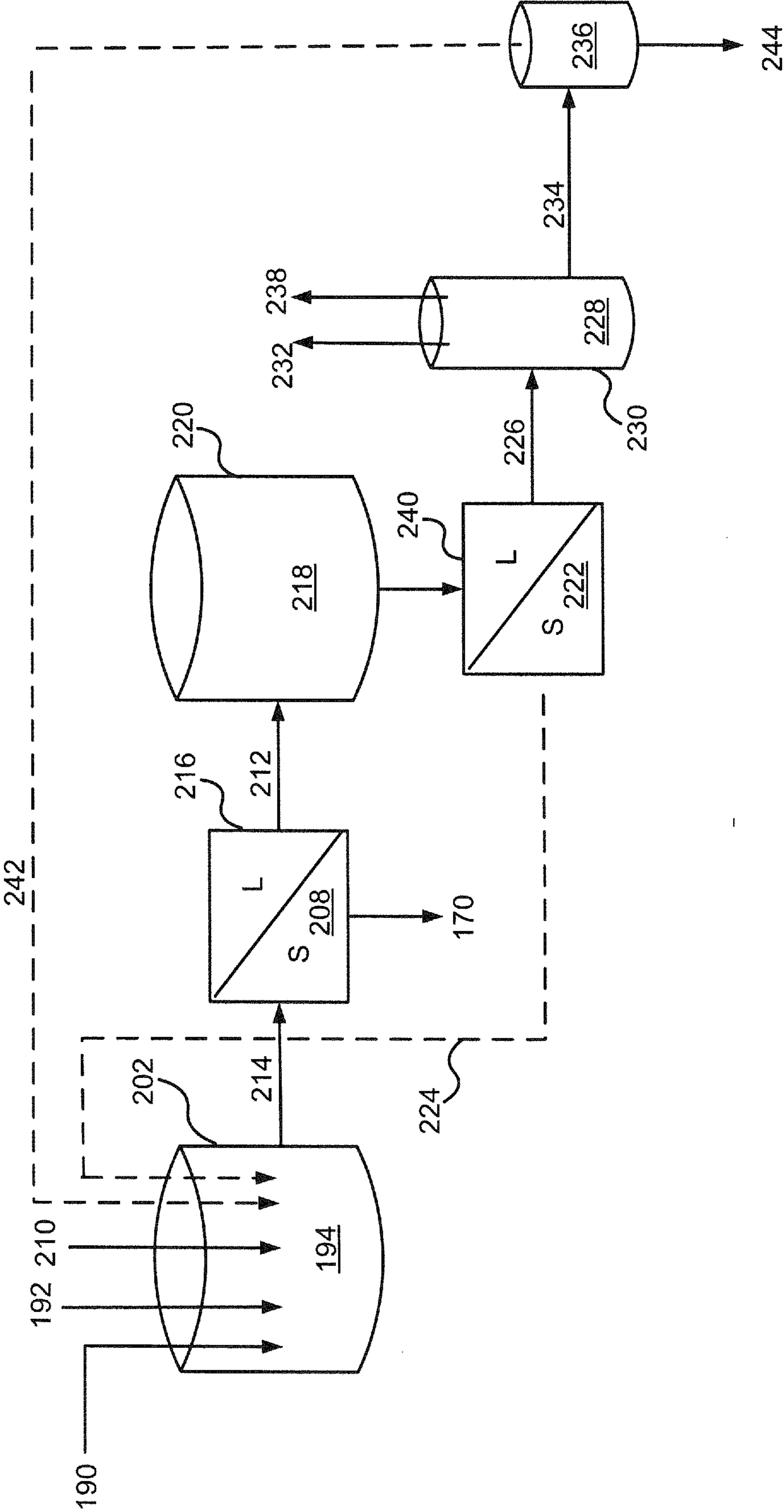


FIG. 7

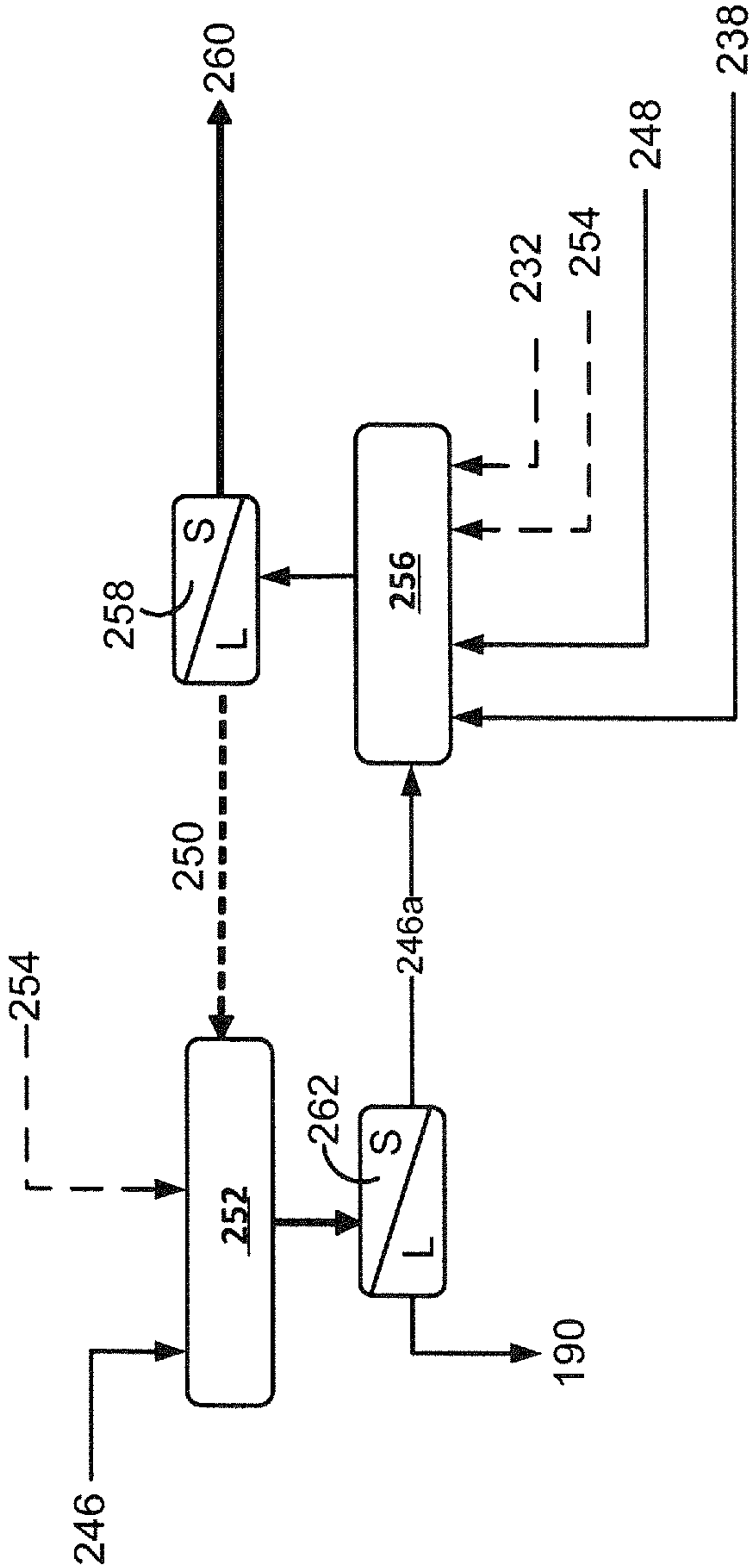


FIG. 8

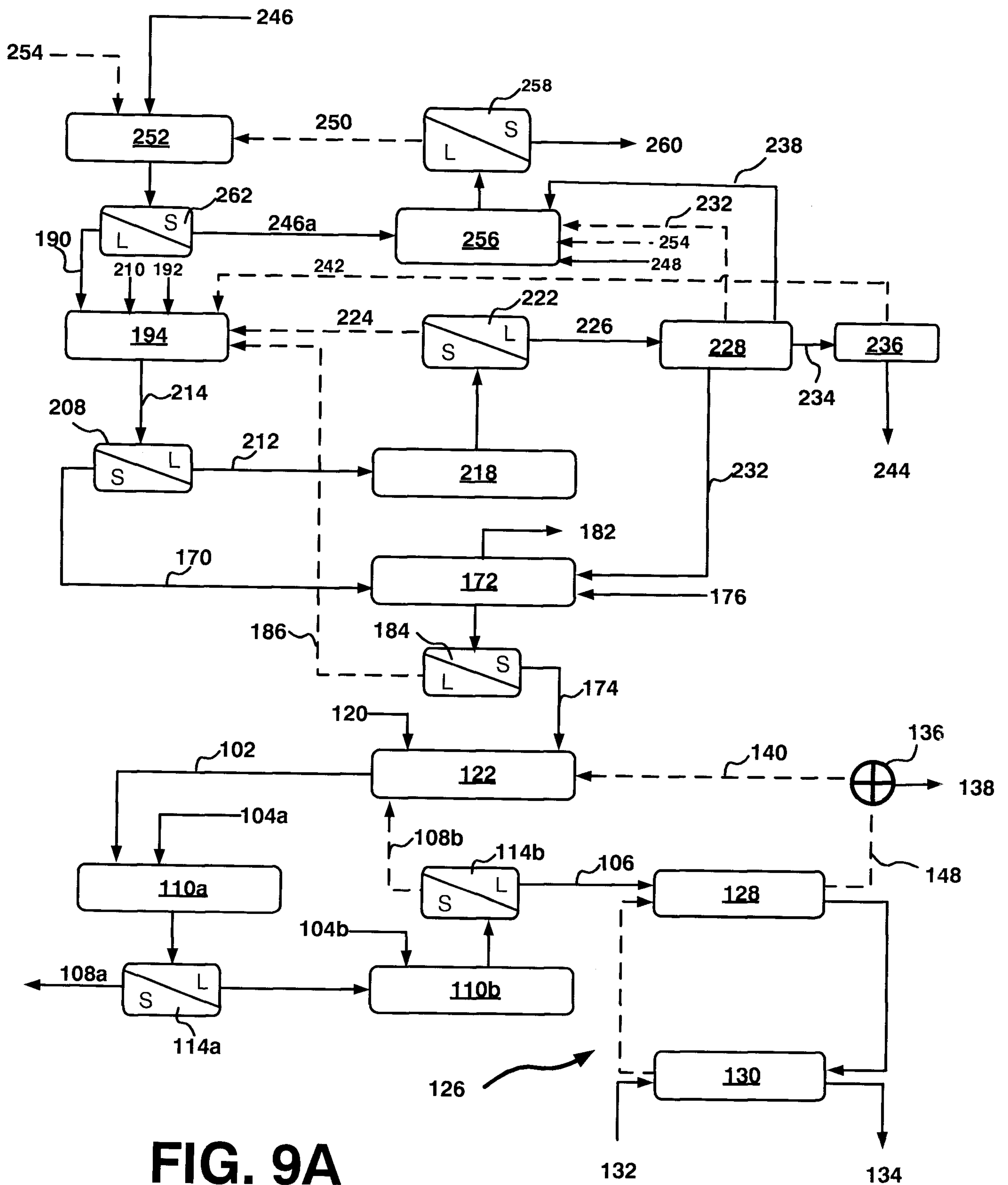
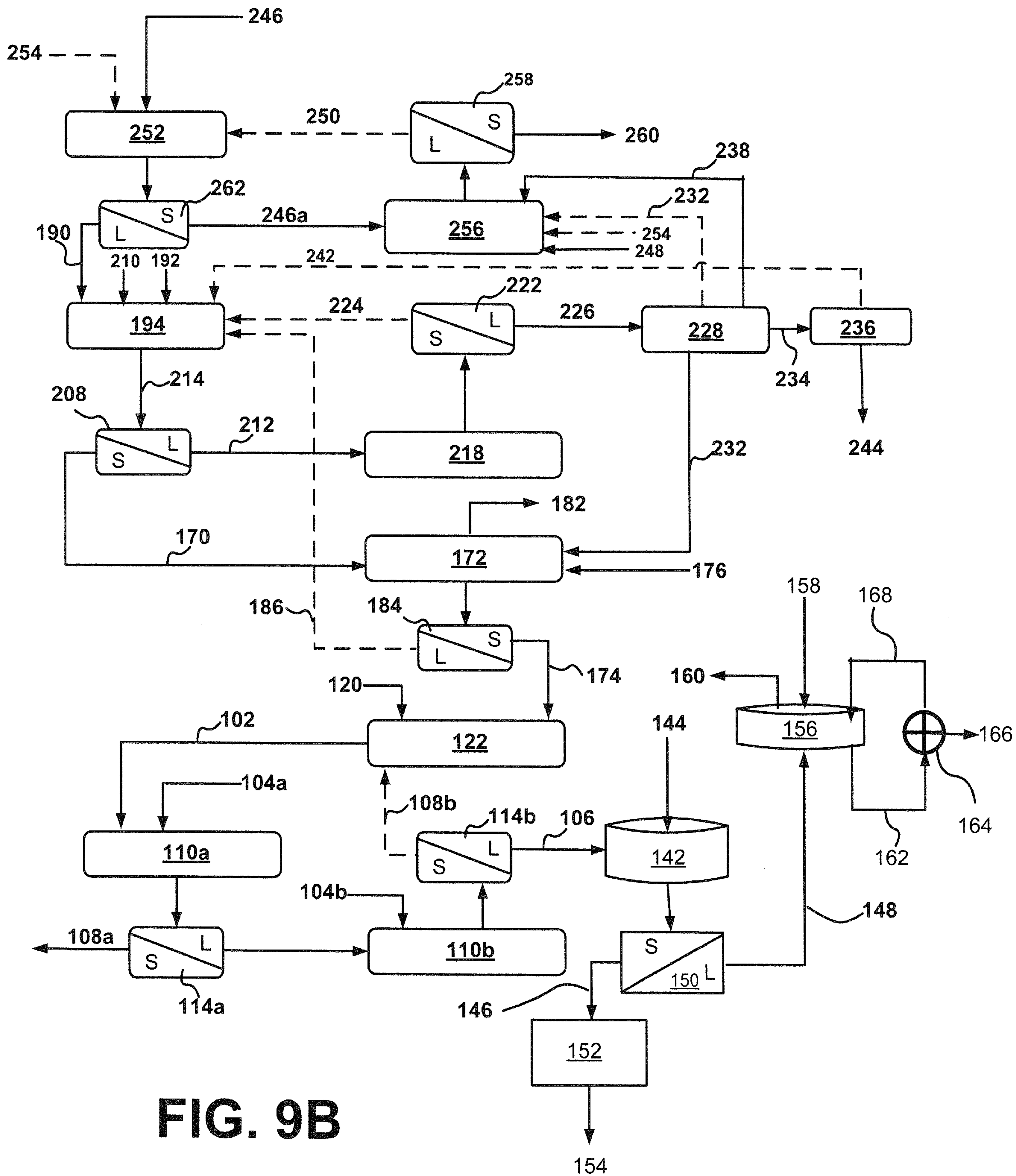


FIG. 9A

**FIG. 9B**

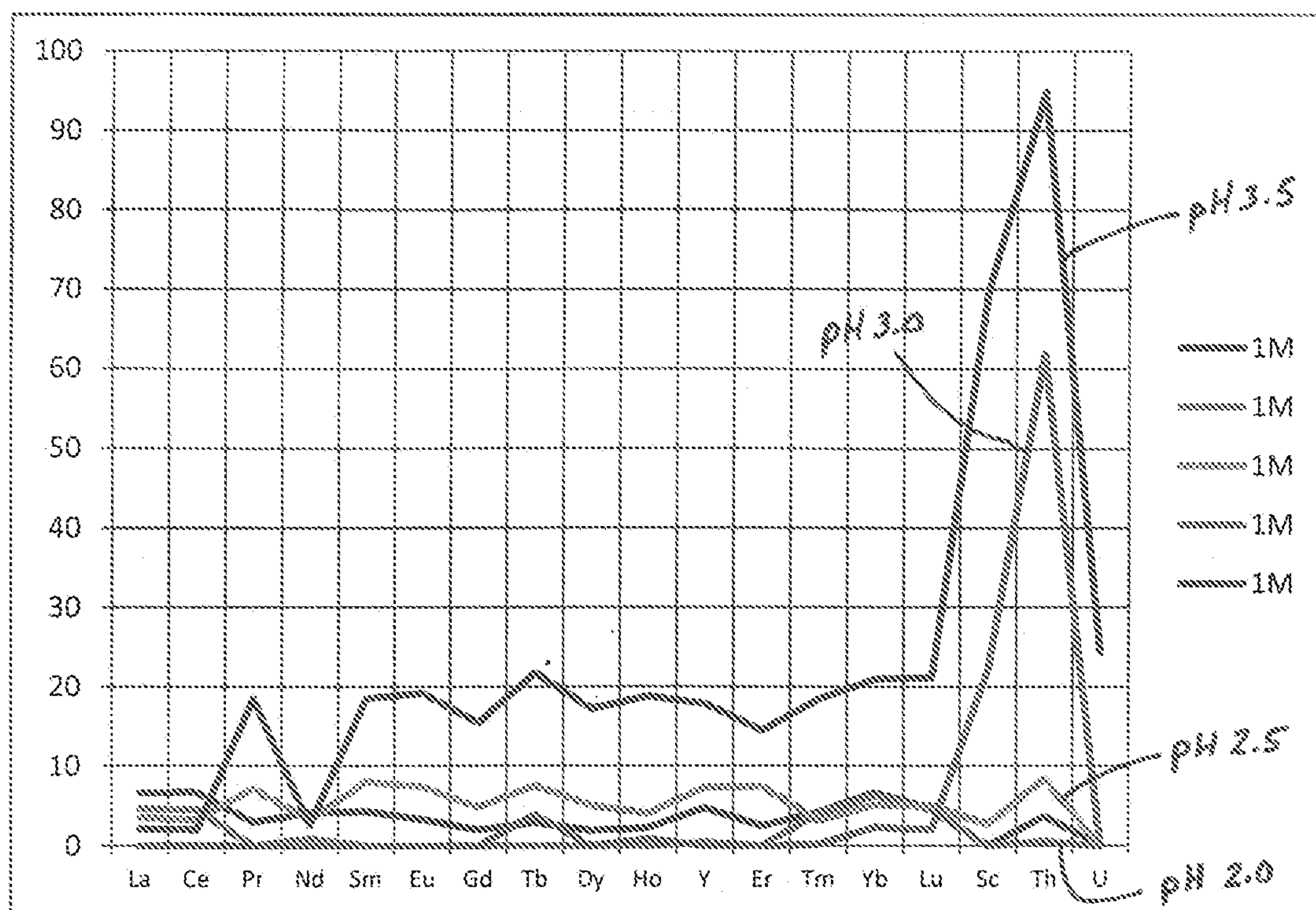


Fig. 10A

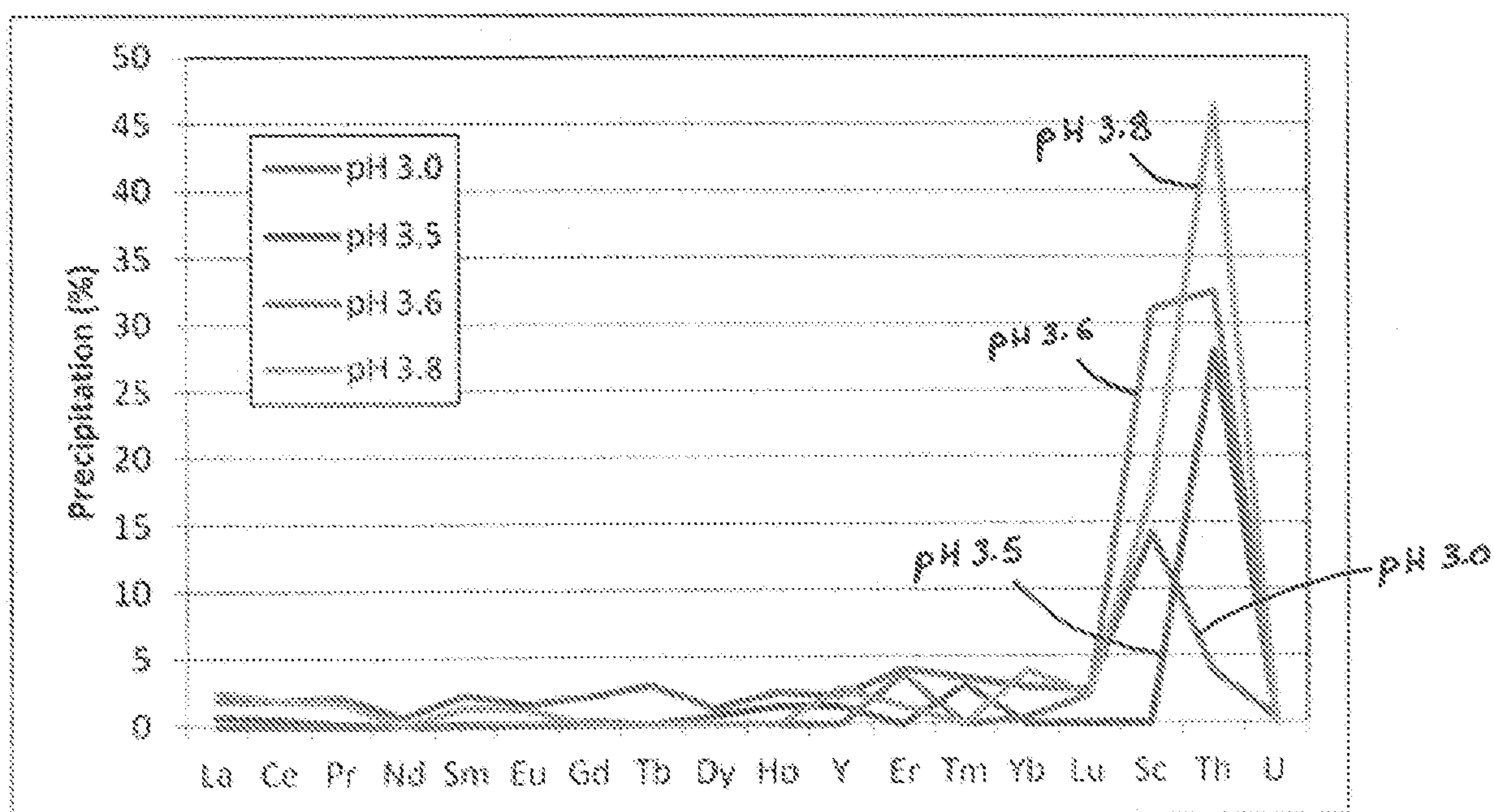


Fig. 10B

