

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

(19) World Intellectual Property

Organization

International Bureau

(43) International Publication Date

07 November 2019 (07.11.2019)



(10) International Publication Number

WO 2019/210367 A1

(51) International Patent Classification:

C22B 59/00 (2006.01)

C22B 3/04 (2006.01)

C22B 3/08 (2006.01)

C01F 17/00 (2006.01)

(21) International Application Number:

PCT/AU2019/050403

(22) International Filing Date:

02 May 2019 (02.05.2019)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

2018901510

03 May 2018 (03.05.2018)

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(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, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, 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, ST, 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).

Published:

— with international search report (Art. 21(3))

(54) Title: PROCESSING RARE EARTH SULPHATE SOLUTIONS

(57) Abstract: A method of processing a purified rare earth sulphate solution, the method including the steps of: contacting the purified rare earth sulphate solution with sodium hydroxide to precipitate rare earths as rare earth hydroxide, including the addition of an oxidant to oxidise cerium contained in the rare earth hydroxide precipitate; and selectively leaching the rare earth hydroxide precipitate with hydrochloric acid to form a rare earth chloride solution and a residue.



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PROCESSING RARE EARTH SULPHATE SOLUTIONS

TECHNICAL FIELD

[0001] The present invention relates generally to the recovery of rare earth elements from rare earth ores or concentrates containing those elements. More particularly, the invention relates to the recovery of separate cerium and cerium free rare earth products from a rare earth sulphate solution, such as a purified rare earth sulphate solution.

[0002] A purified rare earth sulphate solution may for example be one formed from a crude rare earth sulphate derived from the sulphation (acid bake) and subsequent water leach of a monazite ore, concentrate, or associated pre-leach residue, the purified solution may for example be derived from such a crude solution by way of the formation of a rare earth sulphate precipitate followed by a water leach of the precipitate.

BACKGROUND OF THE INVENTION

[0003] Rare earth elements include all the lanthanide elements (lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium), as well as the rare metals scandium and yttrium. For ease of discussion and because of their abundance and similar properties, the Total Rare Earth Elements (TREE) are often divided into three groups; the Light Rare Earths (LRE) which are lanthanum, cerium, praseodymium, and neodymium; the Middle Rare Earths (MRE) which are samarium, europium and gadolinium (promethium does not exist as a stable element); and the Heavy Rare Earths (HRE) which are terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium. Yttrium and Scandium are often added to this list although they are not strictly heavy rare earth elements.

[0004] During the past twenty years there has been an explosion in demand for many items that require rare earth elements, which now include many items that people use every day, such as computer memory, DVD's, rechargeable batteries, mobile phones, catalytic converters, small electric motors, magnets, and fluorescent lighting.

[0005] Rare earth elements also play an essential role in electricity generation from wind power, new generation electric vehicles, and military applications. In this respect, the military uses include night-vision goggles, precision-guided weapons, communications equipment, GPS equipment and batteries.

[0006] The increase in use of rare earth elements in new technology devices has lead to an increase in demand, and a need for diversification in a supply chain that has been dominated by China since the early 1990s. Indeed, the development of non-Chinese resources for the mining and processing of rare earths has expanded in recent years, particularly since China announced in 2010 that it will severely restrict its export of rare earth elements to ensure supply for domestic manufacturing.

[0007] Rare earth containing minerals occurring in nature that are sufficiently rich in rare earth elements to be of current or potential future commercial interest include fluoro-carbonates (such as bastnäsite), fluorides, oxides, phosphates (such as monazite, xenotime, and apatite), and silicates (such as ionic clays and allanite). The world's resources are contained primarily in bastnäsite and monazite. Bastnäsite deposits in China and the United States constitute the largest percentage of the world's known rare-earth economic resources, while monazite deposits in Australia, Brazil, China, India, Malaysia, South Africa, Sri Lanka, Thailand, and the United States constitute the second largest segment.

[0008] Conventional methods for the extraction of rare earth elements from their ores or concentrates are described in the book “*Extractive Metallurgy of Rare Earths*” by C.K. Gupta and N. Krishnamurthy, CRC Press, 2005.

[0009] As outlined in *Gupta and Krishnamurthy (2005)*, rare earth elements have typically been extracted from monazite ores and concentrates by processes of sulphation. In sulphation (also called “acid baking”), the ore or concentrate is mixed with concentrated sulphuric acid and baked at elevated temperatures (such as from 200 to 500°C) to break down the mineral matrix and convert the rare earth elements into sulphate salts that can then be brought into solution by dissolution in a water leach of the baked solids. Once the rare earth elements are in solution, being impure rare earth sulphate solutions that will herein be referred to as “crude rare earth

sulphate solutions”, the rare earth elements are typically recovered by a number of different prior art techniques.

[0010] *Gupta and Krishnamurthy (2005)* also describe processes for the extraction of rare earth elements from bastnäsite ores and concentrates (bastnäsite being a rare earth fluorocarbonate). In China, bastnäsite concentrates are processed by heating with concentrated sulphuric acid to 500°C in a rotary kiln. The residue is then treated with water to dissolve the soluble rare earth sulphates, again forming a crude rare earth sulphate solution.

[0011] One prior art process strategy that has been adopted to recover the rare earth elements contained in such crude rare earth sulphate solutions is to neutralise acid and precipitate problematic impurities, thereby forming “purified” rare earth sulphate solutions, followed by the recovery of the rare earth elements using one of several alternative processes such as solvent extraction, rare earth carbonate precipitation, rare earth oxalate precipitation, rare earth hydroxide precipitation, or ion exchange. Another strategy is to directly recover rare earth elements from crude rare earth sulphate solutions, for which one process option is available in the prior art, namely double sulphate precipitation.

[0012] Many of these process strategies can produce a rare earth hydroxide either directly, as in hydroxide precipitation, or indirectly via caustic conversion of intermediates, such as of double sulphate, carbonate or oxalate. The cerium contained in the resultant rare earth hydroxides can be oxidised with a strong oxidising agent, or by drying in the presence of oxygen at 120 to 150°C. The mixed rare earth hydroxides may then be selectively leached in hydrochloric acid to pH 3 to 4 to produce a rare earth chloride solution and a residue. The problem with existing processes, as described by *Morais et al* in “*Recovery of Cerium by Oxidation/Hydrolysis With $KMNO_4$ - NA_2CO_3* ”, Hydrometallurgy 2003 – Fifth International Conference – Volume 2: Electrometallurgy and Environmental Hydrometallurgy, is that the selective dissolution is very slow and that about 1% of the cerium is leached into the rare earth chloride solution.

[0013] It is an aim of the present invention to provide a effective and efficient process for the selective recovery of rare earth elements from purified rare earth sulphate solutions, and thus ultimately a more economic overall process for producing separated rare earth products from rare earth containing ore.

[0014] The above discussion of background is included to explain the context of the present invention. It is not to be taken as an admission that any of the material referred to was published, known, or part of the common general knowledge (in any country) at the priority date of any one of the claims.

SUMMARY OF THE INVENTION

[0015] As mentioned above, in general terms in rare earth processing, sulphation is where an ore or concentrate is mixed with concentrated sulphuric acid and baked at elevated temperatures to break down the mineral matrix and convert the rare earth elements into sulphate salts that can then be brought into solution by dissolution in a water leach of the baked solids. Once the rare earth elements are in solution, being the so-called "crude" rare earth sulphate solutions, the rare earth elements then require recovery.

[0016] For example, in the applicant's co-pending International patent application lodged on the same day as this application, there is described a method for the precipitation of rare earth sulphate, which includes subjecting a crude rare earth sulphate solution to precipitation in the presence of a water soluble, volatile, organic compound to produce a rare earth sulphate precipitate and an acidic supernatant. The rare earth sulphate precipitate is then washed and dried, and subsequently leached in water to dissolve soluble rare earth sulphate and form a leach solution rich in rare earth sulphate and a leach residue containing impurities in the form of insoluble phosphates. The rare earth sulphate leach solution is then subjected to the precipitation of impurities to form a "purified rare earth sulphate solution" and a purification residue. It is such a "purified" rare earth sulphate solution that the present invention applies to. The present invention could equally be applied to a purified rare earth sulphate prepared by the neutralisation of crude rare earth sulphate such as described in the background.

[0017] The present invention thus provides a method of processing a purified rare earth sulphate solution, the method including the steps of:

- a) contacting the purified rare earth sulphate solution with sodium hydroxide to precipitate rare earths as rare earth hydroxide, including the addition of an oxidant to oxidise cerium contained in the rare earth hydroxide precipitate; and
- b) selectively leaching the rare earth hydroxide precipitate with hydrochloric acid to form a rare earth chloride solution and a residue.

[0018] In one form, in the preparation of a purified rare earth sulphate solution, the washing of a rare earth sulphate precipitate formed from a crude rare earth sulphate solution is conducted with a water-soluble, volatile, organic compound, such as methanol, with the sulphate precipitate then being dried (ideally with volatilised organic recovered and reused) prior to a water leach of the sulphate precipitate. Such a water leach preferably occurs at about 40 °C for up to 180 minutes to dissolve the soluble rare earth sulphate, while leaving most impurities behind as insoluble phosphates (such as thorium) which may be recycled or disposed. Trace quantities of soluble impurities will also be dissolved in such a process.

[0019] Then, following solid-liquid separation, the leach residue may be disposed while the resultant leach solution rich in rare earth sulphate ideally subsequently undergoes a rare earth sulphate purification stage to form the purified rare earth sulphate solution relevant to the present invention and a purification residue.

[0020] In relation to this purification stage, magnesia is preferably added to the rare earth sulphate leach solution to purify that solution by precipitation of impurities, leaving the desired purified rare earth sulphate solution and a purification residue. The purification is ideally operated to maximise the precipitation of impurities while minimising the co-precipitation of rare earth elements. As such, magnesia is preferably dosed over multiple tanks at a temperature up to about 55°C, with a 30 to 120 minute residence time in each tank, to a pH 4.5 to 6.0 end point target. Then, following solid liquid separation, the purification precipitate may be recycled or disposed, and the purified rare earth sulphate solution recovered for further processing.

[0021] Returning to a description of the processing method of the present invention, sodium hydroxide is added to the purified rare earth sulphate solution in order to precipitate the rare earths as rare earth hydroxide, with the addition of the oxidant assisting to oxidise cerium contained in the precipitate. The precipitation step a) is thus ideally operated to maximise the precipitation of rare earth elements and maximise the conversion of cerium (III) to cerium (IV), while minimising the stoichiometric excess of reagent dosing, and minimise the concentration of sulphate in the rare earth hydroxide precipitate.

[0022] The precipitation step a) preferably occurs in a two-stage counter-current process, including a precipitation stage and refining stage, wherein the rare earth sulphate solution feeds into the precipitation stage with spent solution from the refining stage, to precipitate rare earth hydroxide containing sulphate. The sulphate containing rare earth hydroxide may then be converted to clean rare earth hydroxide in the refining stage with the addition of fresh sodium hydroxide.

[0023] In a preferred form, both the precipitation and the refining stage operate at a temperature of 40 to 80°C, and for a time of about 30 to 60 minutes, with the stoichiometry of sodium hydroxide addition being in the range of 100 to 110%, and with 100 to 130% of stoichiometry dosing of oxidant.

[0024] Preferably, the oxidant is hydrogen peroxide and/or sodium hypochlorite, which is added to the precipitation and/or refining stages following sodium hydroxide addition. For the case where hydrogen peroxide is the oxidant, it is preferred that the operating temperature be in the range 50 to 60°C at the point(s) of addition.

[0025] In the leaching step b), the selective leaching of rare earth hydroxide precipitate is preferably conducted in two stages, each stage having multiple tanks and each stage using hydrochloric acid diluted to around 10% w/w using leach solution from the first leach stage. Leach solution from the second leach stage is preferably used to re-pulp, leach rare earth hydroxide precipitate, and to precipitate cerium (IV) that has been dissolved in the second stage, prior to the first leach stage.

[0026] The selective leaching ideally occurs at a temperature of 60 to 80 °C, with the first leach stage being operated to maximise rare earth dissolution while minimising cerium (IV) dissolution, which is achieved with an endpoint pH of about pH

3 to 4, and the second leach stage being operated to minimise the concentration of non-cerium rare earth elements in the residue. In this respect, it is preferred for the rare earth chloride solution to contain negligible cerium, and for the residue to consist primarily of cerium (IV) hydroxide.

[0027] The cerium (IV) hydroxide residue may be packaged as a crude cerium product or further processed to produce a higher purity cerium product. Additionally, barium chloride may subsequently be added to the rare earth chloride solution, with sulphuric acid when sulphate levels are low, to remove radium via co-precipitation with barium sulphate to form a purified rare earth chloride solution. The purified rare earth chloride solution may then be concentrated by evaporation.

[0028] Dilute and/or concentrated purified rare earth chloride may then be separated into two or more different rare earth products by solvent extraction with each rare earth product containing one or more individual rare earth elements.

[0029] The method of the invention may also include some additional steps related to the production of a suitable crude rare earth sulphate solution from a rare earth rich calcium phosphate concentrate, most likely where the rare earth rich calcium phosphate concentrate is a product of the beneficiation of a rare earth containing calcium phosphate rich ore by whole-of-ore flotation. In a preferred form, the ore contains apatite-hosted monazite, and the concentrate contains a higher grade of apatite-hosted monazite relative to the ore.

[0030] In general terms, these pre-processing steps preferably include the pre-leach of a rare earth rich calcium phosphate concentrate with phosphoric acid to form a pre-leach residue enriched in rare earths, the mixing of the pre-leach residue with sulphuric acid with subsequent heating of the mixture to convert the rare earths in the pre-leach residue to water-soluble rare earth sulphates, and finally a water leach of the heated mixture to place the rare earth sulphates in solution and thereby form the crude rare earth sulphate solution suitable for the precipitation step described above.

[0031] The crude rare earth sulphate solution may then be subjected to precipitation in the presence of a water soluble, volatile, organic compound to produce a rare earth sulphate precipitate and an acidic supernatant.

[0032] Ideally, the rare earth sulphate precipitation step is operated to maximise the extent of rare earth precipitation from solution while minimising rare earth precipitation in the form of phosphates and fluorides, and minimising the co-precipitation of impurities. The rare earth sulphate precipitate is expected to contain > 35% TREE, > 12% S, < 2% P, < 0.3% Al, and < 0.5% Fe, while all organic added to the precipitation, less that volatilised, will be contained in the acid supernatant. Indeed, virtually all the water, sulphuric acid, phosphoric acid, Mg, Al, Fe, and U contained in the crude rare earth sulphate solution should be contained in the acidic supernatant.

[0033] While the rare earth sulphate precipitate subsequently undergoes further process steps to form the purified rare earth sulphate solution of the present invention, the acidic supernatant produced may also undergo further process steps aimed at the recovery of the organic compound and the regeneration of phosphoric acid. This may include recovering the organic compound from the acidic supernatant by distillation, resulting in the formation of recovered organic compound and a dilute mixed acid solution, with the recovered organic compound preferably being recycled for use in the precipitation step, and the dilute mixed acid solution being passed on directly and/or following additional concentration by evaporation for use in a phosphoric acid regeneration stage that will also be further described below.

[0034] Following the phosphoric acid pre-leach of the pre-processing stages described above, heat may be applied to the phosphoric acid pre-leach solution, to precipitate out of solution any minor amounts of rare earths as rare earth phosphates, leaving a recovery solution. It is these rare earth phosphates that may then be returned to the sulphation and acid bake steps described above.

[0035] The recovery solution may then be dosed with sulphuric acid and/or the dilute and/or concentrated mixed acid solution of the methanol-stripping stage to convert mono calcium phosphate to phosphoric acid and form a calcium sulphate precipitate which may be disposed. The target is a balance between maximising the reactivity of phosphoric acid and minimising the amount of calcium sulphate precipitate forming in the pre-leach mentioned above.

[0036] The phosphoric acid formed from the recovery solution may then be used as required by the pre-leach in the pre-processing steps described above, and the surplus phosphoric acid may be bled out of the system and forwarded on for phosphoric acid purification.

[0037] In such phosphoric acid purification, impurities (primarily uranium and thorium) in the dilute phosphoric acid bleed may be removed by ion exchange, solvent extraction or any other commercial process along with some rare earth elements. In addition, the concentration of calcium and sulphur in the dilute acid may be adjusted through the addition of sulphuric acid as required to meet consumer specifications. The purified and dilute phosphoric acid may then be concentrated up to generate a phosphoric acid by-product, which may be stored prior to shipment to customers.

DESCRIPTION OF PREFERRED EMBODIMENT

[0038] Figure 1 is a schematic representation of a flow diagram for the precipitation of rare earth sulphates, which also illustrates a preferred pre-processing stage for the rare earth rich calcium phosphates, and a preferred associated phosphoric acid regeneration stage; and

[0039] Figure 2 is a schematic representation of a flow diagram for a preferred embodiment of a method of processing a purified rare earth sulphate solution in accordance with the present invention.

DETAILED DESCRIPTION OF THE FLOW DIAGRAM

[0040] Before providing a more detailed description of a preferred embodiment of the present invention with reference to experimental data, it will be useful to provide some explanation of the flow diagram of Figures 1 and 2.

[0041] Figure 1 shows the precipitation of rare earth sulphates (section A), together with the pre-processing of rare earth rich calcium phosphates (section B) and an associated phosphoric acid regeneration stage (section C). In Figure 2, there is shown a series of rare earth processing stages (section D). It will be appreciated that the focus of the present invention is on the rare earth processing stages in section D.

[0042] Referring firstly to Figure 1, and in process flow order starting with section B, various steps can be seen relating to the production of a suitable crude rare earth sulphate solution 10 from a rare earth rich calcium phosphate concentrate 12, being a product of the beneficiation of a rare earth containing calcium phosphate rich ore by whole-of-ore flotation (not shown).

[0043] These pre-processing steps include the pre-leach of the concentrate with phosphoric acid in a multi stage counter current configuration 14,16 to remove calcium phosphate and to form a pre-leach residue 18 enriched in rare earths and a pre-leach solution 19 containing monocalcium phosphate, impurities and minor amounts of rare earths. In this embodiment, the leach 14,16 is operated at a low temperature (typically 30 to 45 °C), with residence times kept to between 30 to 90 minutes for each stage, and with the overall feed acid to feed concentrate mass ratio kept between 2 and 12 grams of P in the acid per gram of Ca in the concentrate.

[0044] The pre-leach residue 18 is then combined and cracked using concentrated sulphuric acid in a sulphation stage, being mixed 20 with sulphuric acid 22 either at or below an acid bake temperature for a time of up to about 30 minutes to ensure that the resulting mixture is fully homogenised prior to the next steps. Subsequent heating 24 of the mixture converts the rare earths in the pre-leach residue 18 to water-soluble rare earth sulphates 26.

[0045] The water-soluble rare earth sulphates 26 are then cooled to a temperature less than about 50°C over a time period of up to about 300 minutes to remove as much heat out of the sulphated material 26 discharging the acid bake 24 as is practical prior to its use in a subsequent water leach 28.

[0046] The cooled water-soluble rare earth sulphates 27 are then subjected to a water leach 28 to place in solution the rare earth sulphate, phosphoric acid and any remaining sulphuric acid, and thus to form the “crude” rare earth sulphate solution 10 mentioned above and a water leach residue 30 containing insoluble gangue material for disposal.

[0047] Turning now to the next section, section A, being the precipitation of rare earth sulphates, Figure 1 shows the sulphate precipitation stage 32 where the crude rare earth sulphate solution 10 is subjected to precipitation in the presence of a water

soluble, volatile, organic compound (such as methanol) 34 to produce a rare earth sulphate precipitate 36 and an acidic supernatant 38. The sulphate precipitation 32 ideally occurs at a temperature in the range of 60 to 65°C with a residence time in the range of 20 to 40 minutes.

[0048] While the rare earth sulphate precipitate 36 subsequently undergoes further process steps in accordance with the present invention, which will be described below in relation to Figure 2, the acidic supernatant 38 produced in the sulphate precipitation step 32 also undergoes further process steps (section C) aimed at the recovery of the organic compound and the regeneration of phosphoric acid.

[0049] Section C of Figure 1 thus shows recovering the organic compound from the acidic supernatant 38 by distillation 40, resulting in the formation of recovered organic compound 34 and a dilute mixed acid solution 42, with the recovered organic compound 34 being recycled for use in the sulphate precipitation step 32 as the methanol 34, and the dilute mixed acid solution 42 being subjected to additional concentration 44 by evaporation to form a concentrated mixed acid solution 45 for use in a phosphoric acid regeneration stage 46.

[0050] Following the phosphoric acid pre-leach 14,16 mentioned above, heat is applied 48 to the phosphoric acid pre-leach solution 19 to precipitate out of solution any minor amounts of rare earths as rare earth phosphates 50, leaving a recovery solution 52. As can be seen, the rare earth phosphates 50 are then returned to the acid mix 20 and acid bake 24 steps described above. The heating 48 of the phosphoric acid pre-leach solution 19 occurs in several stages of increasing temperatures, the temperatures all being in the range of 60°C to 110°C, with stage residence times of between 60 and 180 minutes.

[0051] The recovery solution 52 is then dosed with sulphuric acid 54 in the acid regeneration stage 46 and, in this embodiment, also with the concentrated mixed acid solution 45, to convert mono calcium phosphate to recoverable phosphoric acid 56 and form a calcium sulphate precipitate 57 which may be disposed. This acid addition 46 is conducted in stages at a temperature of about 40°C and a residence time of between 30 and 60 minutes per stage. Part of the phosphoric acid formed

from the recovery solution 58 is also used by the pre-leach 14,16, while surplus phosphoric acid 59 is bled out of the system.

[0052] Turning now to Figure 2, and the final, inventive, section (section D) of the flow diagram, which shows the rare earth processing stages, this subsequent processing includes washing and drying the rare earth sulphate precipitate (actually shown in Figure 1 as stage 60), and subsequently leaching 62 in water the washed and dried rare earth sulphate precipitate 36 to dissolve soluble rare earth sulphate and form a leach solution 64 rich in rare earth sulphate and a leach residue 66 containing impurities in the form of insoluble phosphates.

[0053] Then, impurities are precipitated 68, with the addition of magnesia 63, from the rare earth sulphate leach solution 64 to form a “purified” rare earth sulphate solution 70 and a purification residue 72, followed by the precipitation 74 of the rare earths in the purified rare earth sulphate solution 70 as rare earth hydroxide precipitate 76.

[0054] Sodium hydroxide 77 is added to the purified rare earth sulphate solution 70 to precipitate the rare earths as rare earth hydroxide 76, with the addition of hydrogen peroxide 78 to oxidise cerium contained in the precipitate. The production of rare earth hydroxide 76 occurs in a two-stage counter current process, with purified rare earth sulphate solution 70 feeding into the precipitation stage (stage one) 74 to precipitate a crude rare earth hydroxide 75 containing some sulphate using spent solution 71 from the refining stage (stage two) 73, with the conversion of rare earth sulphate compounds to rare earth hydroxide compounds occurring with the addition of fresh sodium hydroxide 77 in rare earth hydroxide refining (stage two) 73.

[0055] The rare earth hydroxide precipitate 76 then undergoes selective leaching 79,80,82 with hydrochloric acid to form the rare earth chloride solution 86 and the residue 88 with the rare earth solution 86 containing negligible cerium, and the residue 88 consisting primarily of cerium (IV) hydroxide.

[0056] The selective leaching 79,80,82 of the rare earth hydroxide precipitate 76 is conducted in a multi stage configuration, with hydrochloric acid diluted to 10% w/w using polished stage one 80 leach solution prior to its addition to stage one 80 and

stage two 82 leach tanks, over multiple tanks in each stage, and stage two 82 solution is used to re-pulp and leach rare earth hydroxide cake prior to stage one 80 leach.

[0057] The cerium (IV) hydroxide residue 88 is then packaged as a crude cerium product, while the rare earth chloride solution 86 is dosed with barium chloride 90 to remove radium via co-precipitation with barium sulphate and form a purified rare earth chloride solution 92. The purified rare earth chloride solution 92 is then concentrated by evaporation 94.

DESCRIPTION OF EXPERIMENTAL DATA

[0058] Attention will now be directed to a description of experimental data across the entire flowsheet, developed to illustrate a preferred embodiment of the present invention.

Rare Earth Sulphate Precipitation

[0059] Rare earth sulphate precipitation tests were conducted by contacting a measured quantity of pre-heated water leach solution with a measured quantity of ambient temperature methanol in a suitable well agitated baffled vessel fitted with reflux condenser to minimise evaporative loss. The resulting mixture was maintained at a setpoint temperature for a specified duration, then vacuum filtered. The filter cake was then washed thoroughly with methanol to remove entrained solution prior to drying.

The influence of temperature (Tests 1 and 2)

[0060] Two rare earth sulphate precipitation tests were conducted to evaluate the influence of reaction temperature on performance. One test was conducted at 60 to 65 °C (Test 1) while the other was conducted at 40 to 45 °C. Both tests were conducted on the same water leach solution (Table 1) and were contacted with 1 gram of methanol per gram of water leach solution for 30 minutes. The results are summarised in Tables 2 to 4. The results indicate that operating at lower temperatures results in reduced Al, P, Fe, Th, and U co-precipitation with rare earth sulphate.

Table 1: Feed solution composition

Test	LRE	MRE	HRE	Y	TRE	Al	P	S	Ca	Fe	Th	U
	g/L	mg/L	mg/L	mg/L	g/L	g/L	g/L	g/L	mg/L	g/L	g/L	mg/L
1 & 2	15.0	710	90	130	15.9	2.69	33.2	76.5	339	3.32	1.59	156

Table 2: Final solution composition

Test	LRE	MRE	HRE	Y	TRE	Al	P	S	Ca	Fe	Th	U
	mg/L	mg/L	mg/L	mg/L	mg/L	g/L	g/L	g/L	mg/L	g/L	g/L	mg/L
1	427	92	28	64	610	1.46	19.2	39.6	73	1.80	660	77
2	474	95	28	63	659	1.39	18.6	39.6	56	1.77	710	77

Table 3: Rare earth sulphate precipitate composition (% w/w or g/t)

Test	LRE	MRE	HRE	Y	TRE	Al	P	S	Ca	Fe	Th	U
	%	%	g/t	g/t	%	g/t	%	%	%	g/t	%	g/t
1	40.3	1.21	611	757	41.6	476	0.23	14.1	0.41	629	0.76	1.6
2	40.7	1.17	514	637	42.0	424	0.18	14.1	0.46	559	0.47	1.2

Table 4: Precipitation extent (%)

Test	LRE	MRE	HRE	Y	TRE	Al	P	S	Ca	Fe	Th	U
1	94.8	71.7	29.9	18.7	92.9	0.6	0.2	6.4	52.3	0.7	18.1	0.0
2	94.0	69.1	25.1	15.6	92.1	0.6	0.2	6.1	59.7	0.6	10.7	0.0

The influence of contact ratio and residence time (Tests 3 to 9)

[0061] Two sets of rare earth sulphate precipitation tests were conducted to evaluate the influence of organic to aqueous contact ratio and residence time on performance. Four contact ratios (0.25, 0.5, 0.75, and 1) were tested in the first set of tests (Tests 3 to 6 respectively). Subsamples were collected at 30, 60, and 120 minutes (subsamples A, B, and C) in each of the tests 3 to 6. The second set of tests (Tests 7 to 9) evaluated shorter residence times (10, 20, and 30 minutes respectively) with a contact ratio of 1 using a different feed solution to the first set (see Table 5). All tests (Tests 3 to 9) used methanol as the organic phase, and were conducted with a 60 to 65 °C temperature target while experienced temperatures ranging between 55 to 70 °C. The results are summarised in Tables 6 to 8.

[0062] The results indicate that operating at lower organic to aqueous contact ratios reduces the rare earth element precipitation extent. The results indicate that rare earth sulphate precipitation is effectively complete within the shortest residence time tested (10 minutes in Test 7), while the precipitation of impurities such as thorium are effectively complete by 20 minutes, with negligible additional precipitation observed with extended contact durations.

Table 5: Feed solution composition

Test	LRE	MRE	HRE	Y	TRE	Al	P	S	Ca	Fe	Th	U
	g/L	mg/L	mg/L	mg/L	g/L	g/L	g/L	g/L	mg/L	g/L	g/L	mg/L
3-6	29.2	1048	162	241	30.7	3.3	14.4	53.4	950	3.0	2.33	235
7-9	24.6	890	115	205	25.8	4.0	14.1	40.4	1220	2.4	1.90	168

Table 6: Final solution composition

Test	LRE	MRE	HRE	Y	TRE	Al	P	S	Ca	Fe	Th	U
	mg/L	mg/L	mg/L	mg/L	mg/L	g/L	g/L	g/L	mg/L	g/L	g/L	mg/L
3A	274	89	39	86	488	1.5	6.01	19.3	130	1.3	0.91	106
3B	291	90	40	87	508	1.5	6.04	19.1	140	1.4	0.93	107
3C	264	90	40	91	485	1.6	6.18	18.7	140	1.5	0.97	113

Test	LRE	MRE	HRE	Y	TRE	Al	P	S	Ca	Fe	Th	U
4A	674	106	43	96	919	1.7	7.08	23.3	170	1.6	1.01	121
4B	782	107	45	98	1032	1.7	7.23	24.2	180	1.6	1.05	126
4C	588	97	42	94	821	1.7	6.79	22.0	170	1.6	0.96	121
5A	1721	211	65	133	2130	2.1	8.23	25.8	250	1.9	1.29	147
5B	1839	222	67	141	2269	2.2	8.78	29.8	260	1.9	1.38	154
5C	2544	248	73	151	3016	2.3	9.43	32.2	300	2.1	1.50	162
6A	5721	457	100	176	6453	2.6	10.4	37.0	520	2.4	1.80	184
6B	5287	448	100	186	6021	2.7	10.4	35.2	530	2.4	1.86	186
6C	7265	498	106	193	8062	2.8	11.0	36.4	570	2.6	1.98	191
7	389	56	24	58	527	1.7	6.05	14.2	80	1.1	0.39	75
8	443	58	23	57	580	1.7	6.20	16.3	< 50	1.0	0.28	75
9	394	52	22	54	523	1.8	6.29	16.8	< 50	1.0	0.27	78

Table 7: Rare earth sulphate precipitate composition (% w/w or g/t)

Test	LRE	MRE	HRE	Y	TRE	Al	P	S	Ca	Fe	Th	U
	%	%	g/t	g/t	%	g/t	%	%	%	g/t	%	g/t
3A	40.7	1.19	695	1030	42.1	106	0.37	14.8	0.74	769	1.06	5.1
3B	40.5	1.18	682	1000	41.8	106	0.37	14.9	0.77	769	1.01	4.7
3C	40.6	1.17	698	1020	41.9	106	0.38	14.9	0.80	769	1.06	5.5
4A	40.4	1.21	801	1260	41.9	212	0.41	14.9	0.77	839	1.16	7.5
4B	39.2	1.16	755	1140	40.5	212	0.39	14.7	0.76	839	1.08	6.0
4C	39.5	1.18	758	1140	40.9	159	0.41	14.8	0.80	839	1.16	5.4
5A	40.3	1.06	576	826	41.5	106	0.40	14.9	0.76	769	0.94	6.0
5B	39.5	1.09	567	801	40.7	53	0.39	14.8	0.73	769	0.93	4.5
5C	39.8	1.08	570	800	41.0	53	0.40	14.8	0.77	699	0.94	5.3
6A	41.0	0.90	369	473	42.0	< 53	0.35	14.7	0.49	490	0.62	2.0
6B	40.3	0.88	355	453	41.2	< 53	0.34	14.7	0.47	560	0.60	2.1

Test	LRE	MRE	HRE	Y	TRE	Al	P	S	Ca	Fe	Th	U
6C	40.8	0.87	355	461	41.7	< 53	0.38	14.7	0.55	525	0.58	2.5
7	38.9	1.21	881	1350	40.3	1641	1.21	14.1	1.52	2238	2.12	30
8	37.9	1.20	939	1440	39.3	2487	1.89	13.6	1.65	3567	2.65	53
9	38.1	1.26	997	1590	39.6	2540	1.89	13.7	1.67	3357	2.74	52

Table 8: Precipitation extent (%)

Test	LRE	MRE	HRE	Y	TRE	Al	P	S	Ca	Fe	Th	U
3A	97.8	80.3	35.3	26.8	96.3	0.2	1.9	18.9	63.6	1.8	26.2	0.1
3B	97.8	80.4	35.1	26.4	96.3	0.2	1.9	19.6	63.3	1.7	25.3	0.1
3C	98.1	81.4	36.6	27.2	96.7	0.2	2.0	21.0	65.7	1.7	26.9	0.2
4A	95.5	80.0	39.4	31.5	94.1	0.4	2.0	18.3	61.4	1.8	28.7	0.2
4B	94.7	79.6	37.8	29.5	93.4	0.4	1.9	18.0	60.2	1.9	27.0	0.2
4C	96.3	82.3	41.1	31.7	95.0	0.4	2.3	20.4	64.3	2.0	31.7	0.2
5A	90.3	66.7	26.1	19.8	88.6	0.2	1.9	18.7	54.6	1.6	22.4	0.2
5B	89.7	66.4	25.3	18.6	87.9	0.1	1.8	16.7	53.1	1.6	21.4	0.1
5C	87.0	65.0	25.0	18.5	85.3	0.1	1.8	16.5	52.2	1.4	21.1	0.1
6A	72.9	42.4	12.2	9.2	71.0	-	1.2	13.0	26.3	0.8	11.5	0.0
6B	76.7	46.0	13.4	9.5	74.8	-	1.4	15.3	27.8	1.0	12.2	0.0
6C	69.3	41.3	11.9	8.7	67.5	-	1.4	14.0	27.8	0.8	10.5	0.1
7	96.7	86.1	52.0	40.3	95.7	2.7	5.5	22.4	84.6	5.6	61.3	1.2
8	96.2	86.1	54.8	43.2	95.3	4.2	8.3	19.9	-	9.6	73.9	2.1
9	96.7	88.1	57.7	47.4	95.9	4.1	8.4	20.0	-	9.3	75.5	2.0

The influence of feed composition (Tests 10 to 24)

[0063] Fifteen rare earth sulphate precipitation tests were conducted to evaluate the influence of variation in feed composition on precipitation performance. Each test used a different crude rare earth sulphate feed solution (Table 9), was contacted with

methanol with a 1 to 1 w/w contact ratio for 30 minutes, with a 60 to 65 °C temperature target while experienced temperatures ranging between 55 to 70 °C. The results are summarised in Tables 10 to 12, from which it can be seen that most tests resulted in a relatively clean rare earth sulphate precipitate with some variation in iron aluminium and phosphate co-precipitation.

[0064] To understand this impurity co-precipitation, the results have been condensed down and sequenced according to the free sulphuric acid content of crude rare earth sulphate feed solution for each test (Table 13). This free acid value is a calculated value for convenience and may not reflect the actual speciation which takes place in the feed solution. The free acid content was determined by summing up all the cations and anions measured and inferred from solution assay result with the concentration of protons calculated to balance cations and anions. It was then assumed that all phosphate is present as phosphoric acid with remaining protons assigned as sulphuric acid.

[0065] For Test 13 this resulted in a negative content of sulphuric acid which suggests that either the phosphate is not fully protonated or that assay uncertainty has biased cations over anions. Either way, Test 13 is low on free acid, and a significant fraction of the precipitating rare earth elements have precipitated as phosphates. Overall the results suggest that in order to minimise the precipitation of rare earth elements as phosphates, the from phosphate containing crude rare earth sulphate solution should contain 5 % w/w or more free H₂SO₄ as it has been defined here.

Table 9: Feed solution composition

Test	LRE	MRE	HRE	Y	TRE	Al	P	S	Ca	Fe	Th	U
	g/L	mg/L	mg/L	mg/L	g/L	g/L	g/L	g/L	mg/L	g/L	g/L	mg/L
10	13.4	508	73	122	14.1	0.9	6.25	24.8	1180	0.80	0.78	110
11	11.8	449	64	108	12.4	1.7	11.2	51.3	1043	1.28	0.69	97
12	20.7	625	79	155	21.6	7.6	31.3	50.4	810	4.90	2.24	193
13	20.8	684	85	163	21.7	12.1	40.1	25.4	3320	3.30	1.17	167
14	27.7	985	131	233	29.1	8.0	29.5	47.9	850	3.80	2.47	222

Test	LRE	MRE	HRE	Y	TRE	Al	P	S	Ca	Fe	Th	U
15	27.6	1073	153	232	29.0	5.39	37.9	112	420	4.71	2.35	228
16	34.1	1424	167	288	35.9	3.83	26.6	99.7	818	3.41	3.48	307
17	32.8	1323	158	267	34.5	3.23	23.8	91.6	573	2.37	3.29	285
18	34.2	1534	170	332	36.3	2.65	24.8	106	575	3.96	3.73	338
19	22.5	802	116	204	23.6	1.58	31.4	95.0	720	0.59	2.24	197
20	24.6	907	130	233	25.9	1.71	33.2	106	525	0.91	2.51	225
21	15.5	574	109	224	16.4	2.21	39.4	129	306	1.40	2.86	265
22	9.62	345	85	186	10.2	2.84	44.4	157	147	2.30	3.35	319
23	8.69	245	65	149	9.14	3.52	51.2	184	94	3.29	3.76	367
24	15.4	493	64	123	16.1	6.89	48.0	89.5	464	5.25	1.81	169

Table 10: Final solution composition

Test	LRE	MRE	HRE	Y	TRE	Al	P	S	Ca	Fe	Th	U
	mg/L	mg/L	mg/L	mg/L	mg/L	g/L	g/L	g/L	mg/L	g/L	mg/L	mg/L
10	189	21	11	28	250	0.3	2.01	8.51	80	0.3	68	49.8
11	269	49	17	35	371	0.7	4.52	20.1	230	0.5	353	43.5
12	590	52	17	45	704	3.5	12.4	16.5	100	1.9	617	83.4
13	104	15	6	19	144	3.7	13.3	8.87	110	0.6	20	53.3
14	413	37	16	42	509	2.4	10.8	15.0	< 50	1.5	414	80.6
15	280	87	36	67	468	2.5	17.5	45.3	125	2.17	817	99.0
16	392	71	30	69	563	1.58	10.7	36.0	190	1.38	923	125
17	290	35	22	55	401	1.29	9.97	34.5	100	0.97	816	130
18	393	82	39	83	597	1.03	11.1	44.1	120	1.63	1165	159
19	354	59	24	56	494	0.63	13.8	39.7	108	0.25	629	81.6
20	320	68	27	62	478	0.72	15.0	45.6	87	0.39	692	86.6
21	366	68	28	65	526	0.88	17.4	5.24	64	0.56	896	102
22	345	52	22	54	472	0.93	18.4	5.06	28	0.75	937	102

Test	LRE	MRE	HRE	Y	TRE	Al	P	S	Ca	Fe	Th	U
23	477	49	20	50	596	1.37	24.6	7.16	10	1.26	1275	134
24	441	60	17	40	557	3.09	23.8	3.52	55	2.21	732	71.9

Table 11: Rare earth sulphate precipitate composition (% w/w or g/t)

Test	LRE	MRE	HRE	Y	TRE	Al	P	S	Ca	Fe	Th	U
	%	%	g/t	g/t	%	%	%	%	%	%	%	g/t
10	35.8	1.22	1172	1890	37.3	0.11	1.62	14.2	2.12	0.21	2.24	45
11	38.1	1.08	670	932	39.4	0.005	0.29	15.3	1.44	0.05	0.79	2.6
12	38.8	1.01	706	1190	39.9	0.15	1.66	13.6	1.33	0.16	1.90	29
13	24.3	0.77	799	1410	25.3	3.38	11.4	7.21	3.58	2.20	3.35	410
14	36.5	1.24	964	1510	38.0	0.12	1.73	12.4	0.97	0.17	2.42	19
15	40.0	1.18	712	1050	41.4	<0.005	0.22	14.7	0.32	0.06	0.61	1.4
16	40.1	1.23	910	1470	41.6	0.005	0.23	14.6	0.49	0.06	1.24	3.6
17	40.1	1.28	1225	2200	41.7	0.005	0.24	14.6	0.44	0.06	1.70	4.5
18	39.7	1.38	1056	1670	41.4	<0.005	0.21	14.5	0.40	0.07	1.53	5.4
19	40.1	1.22	865	1360	41.6	<0.005	0.28	14.9	0.73	0.04	1.17	2.9
20	41.7	1.29	926	1430	43.2	<0.005	0.25	14.8	0.41	0.04	1.15	2.2
21	41.8	1.17	979	1550	43.3	<0.005	0.23	14.7	0.29	0.04	1.44	2.4
22	41.2	0.97	898	1520	42.4	<0.005	0.23	14.7	0.18	0.05	1.88	2.4
23	40.9	0.68	596	1040	41.7	<0.005	0.25	15.0	0.30	0.05	1.66	7.0
24	39.7	0.88	498	787	40.7	0.02	0.73	14.7	0.93	0.06	0.51	5.5

Table 12: Precipitation extent (%)

Test	LRE	MRE	HRE	Y	TRE	Al	P	S	Ca	Fe	Th	U
10	96.3	88.8	60.3	48.2	95.4	4.9	10.0	18.8	78.6	8.8	82.0	1.2
11	94.6	73.3	32.4	24.7	93.0	0.1	0.8	8.7	43.7	1.2	21.7	0.1
12	93.3	80.5	46.8	36.1	92.4	0.9	2.8	15.0	73.9	1.8	39.7	0.7
13	98.8	94.6	81.3	72.1	98.4	23.8	22.7	21.8	91.8	55.7	98.3	20.9
14	95.8	89.5	60.4	48.0	95.1	1.3	4.0	17.7	-	2.9	60.2	0.6
15	97.5	78.4	34.8	29.5	95.9	-	0.3	8.0	40.7	0.7	16.5	0.0
16	96.5	82.3	44.9	36.4	95.2	0.1	0.6	9.8	41.1	1.1	26.5	0.1
17	97.6	91.6	62.2	54.0	96.8	0.1	0.7	11.1	56.6	1.7	38.0	0.1
18	96.5	82.3	43.1	35.7	95.0	-	0.5	8.4	48.0	1.2	26.7	0.1
19	96.1	81.7	43.7	34.7	94.8	-	0.4	7.6	59.5	3.5	28.8	0.1
20	96.8	81.2	43.8	34.5	95.4	-	0.4	6.9	51.8	2.4	27.6	0.1
21	94.0	70.2	32.1	24.6	91.8	-	0.2	3.7	37.9	0.8	18.0	0.0
22	89.1	56.1	21.7	16.2	86.0	-	0.1	1.9	30.3	0.4	12.0	0.0
23	85.6	49.2	17.0	12.7	82.9	-	0.1	1.4	67.6	0.3	8.3	0.0
24	92.9	68.3	30.0	22.5	91.4	0.1	0.4	5.7	71.1	0.4	9.2	0.1

Table 13: Rare earth sulphate composition and precipitation extents as a function of free acid

Test	Feed Free Acid	Precipitate Composition (% w/w)				Precipitation Extent (%)			
	% w/w H ₂ SO ₄	TREE	P	Al	Fe	TREE	P	Al	Fe
13	-2.5	25.3	11.4	3.38	2.20	98.4	22.7	23.8	55.7
10	4.3	37.3	1.62	0.11	0.21	95.4	10.0	4.9	8.8
14	4.5	38.0	1.73	0.12	0.17	95.1	4.0	1.3	2.9
12	5.7	39.9	1.66	0.15	0.16	92.4	2.8	0.9	1.8
11	9.9	39.4	0.29	0.005	0.05	93.0	0.8	0.1	1.2

Test	Feed Free Acid	Precipitate Composition (% w/w)				Precipitation Extent (%)			
24	13.7	40.7	0.73	0.02	0.06	91.4	0.4	0.1	0.4
17	14.8	41.7	0.24	0.005	0.06	96.8	0.7	0.1	1.7
16	15.9	41.6	0.23	0.005	0.06	95.2	0.6	0.1	1.1
19	16.1	41.6	0.28	<0.005	0.04	94.8	0.4	-	3.5
18	16.9	41.4	0.21	<0.005	0.07	95.0	0.5	-	1.2
15	17.7	41.4	0.22	<0.005	0.06	95.9	0.3	-	0.7
20	17.7	43.2	0.25	<0.005	0.04	95.4	0.4	-	2.4
21	21.3	43.3	0.23	<0.005	0.04	91.8	0.2	-	0.8
22	25.2	42.4	0.23	<0.005	0.05	86.0	0.1	-	0.4
23	28.1	41.7	0.25	<0.005	0.05	82.9	0.1	-	0.3

Phosphoric Acid Pre-Leach

[0066] Pre-leach tests were conducted by contacting a measured quantity of temperature controlled phosphoric acid solution with a measured quantity of concentrate in a suitable well agitated baffled vessel. The resulting mixture was maintained at a setpoint temperature for a specified duration, then vacuum filtered. The filter cake was then washed thoroughly with DI water to remove entrained solution prior to drying.

The influence of concentrate feed variability

[0067] Five pre-leach tests were conducted to evaluate the influence of variability in the feed concentrate composition (Table 14) on the performance of pre-leach. Each test was conducted using the same feed acid (Table 15), with an acid to concentrate contact ratio of 8.4 grams of P in acid per gram of Ca in the concentrate, at 30 °C for two hours. The results are summarised in Table 16.

Table 14: Feed concentrate composition (% w/w or g/t)

Test	LRE	MRE	HRE	TRE	Mg	Al	P	S	Ca	Fe	Th	U
	%	%	g/t	%	%	%	%	%	%	%	%	g/t
24	5.30	0.21	365	5.62	0.25	1.47	12.8	0.24	29.3	1.24	0.48	355
25	5.19	0.20	356	5.50	0.07	1.37	13.0	0.19	29.3	2.11	0.49	395
26	3.71	0.14	227	3.92	0.37	1.01	11.2	0.13	31.7	0.67	0.44	217
27	5.50	0.21	387	5.83	0.04	4.18	11.7	0.07	22.4	0.44	0.57	415
28	5.87	0.22	348	6.19	0.01	0.08	16.0	0.24	34.6	0.25	0.90	373

Table 15: Feed acid composition (g/L or mg/L)

Test	LRE	MRE	HRE	TRE	Mg	Al	P	S	Ca	Fe	Th	U
	mg/L	mg/L	mg/t	mg/L	g/L	g/L	g/L	mg/L	g/L	g/L	mg/L	mg/L
24 to 28	0.3	-	-	0.4	6.7	6.6	207	< 10	4.3	6.2	0.4	<0.001

Table 16: Dissolution extent (%)

Test	LRE	MRE	HRE	TRE	Mg	Al	P	S	Ca	Fe	Th	U
24	36.6	42.9	47.2	37.1	76.5	9.0	83.2	22.8	87.1	11.6	38.0	31.0
25	34.8	45.4	52.1	35.5	44.3	2.8	83.7	85.8	84.0	1.6	32.7	38.4
26	72.4	74.4	75.1	72.5	17.0	9.7	87.5	87.3	86.8	11.7	74.1	76.0
27	18.4	27.1	34.8	19.1	46.8	16.6	63.1	59.3	72.0	3.8	46.3	26.1
28	38.5	43.1	49.9	38.8	41.4	17.0	83.1	89.1	87.5	0.7	27.7	34.5

The influence of feed acid composition

[0068] Five pre-leach tests were conducted to evaluate the influence of variability in the feed acid composition (Table 17) on the performance of pre-leach. Each test was conducted using the same feed concentrate (Table 18), with an acid to

concentrate contact ratio of 13 grams of acid per gram of feed concentrate, at 30 °C for two hours. The results are summarised in Table 19.

Table 17: Feed acid composition (% w/w or g/t)

Test	LRE	MRE	HRE	TRE	Mg	Al	P	S	Ca	Fe	Th	U
	mg/L	mg/L	mg/L	mg/L	g/L	g/L	g/L	mg/L	g/L	g/L	mg/L	mg/L
29	50.3	-	-	50.4	3.7	3.6	176	< 10	4.7	3.4	< 0.1	< 0.1
30	47.1	-	-	47.3	7.4	7.2	181	< 10	4.9	6.9	1.2	< 0.1
31	40.3	-	-	40.6	13.3	7.0	174	< 10	4.9	6.3	< 0.1	< 0.1
32	30.0	-	-	30.2	7.2	10.9	182	510	5.0	6.8	< 0.1	< 0.1
33	36.0	-	-	36.2	7.2	7.3	177	< 10	4.9	3.3	< 0.1	< 0.1

Table 18: Feed concentrate composition (% w/w or g/t)

Test	LRE	MRE	HRE	TRE	Mg	Al	P	S	Ca	Fe	Th	U
	%	%	g/t	%	%	%	%	%	%	%	%	g/t
29 to 33	5.57	0.22	392	5.90	0.23	1.32	13.1	0.23	30.1	1.16	0.51	377

Table 19: Dissolution extent (%)

Test	LRE	MRE	HRE	TRE	Mg	Al	P	S	Ca	Fe	Th	U
29	31.2	36.7	46.3	31.7	80.4	0	85.2	90.5	90.1	6.9	31.2	25.7
30	30.1	35.3	41.9	30.5	81.0	3.3	74.5	82.9	79.4	8.4	31.6	26.2
31	25.2	27.6	32.9	25.5	79.5	0.3	63.0	72.7	68.1	6.2	26.9	19.9
32	29.4	31.9	37.9	29.7	80.8	2.0	69.1	77.2	74.0	7.8	32.2	23.5
33	31.6	32.1	38.4	31.8	80.9	1.6	76.3	84.3	81.2	7.9	33.5	25.0

Continuous two stage counter current leach

[0069] A continuous two-stage pre-leach circuit test was conducted (Test 34). For this test, a thickener was used for first stage solid liquid separation, while thickening with filtration of thickener underflow was used for solid liquid separation in the second stage. The first stage featured a single tank with 30 minute residence time operated at 40 to 45 °C, while the second stage contained two 30 minute residence time tanks operated at 30 °C. Stage one thickener underflow fed into the first stage two leach tank along with phosphoric acid (Table 20). Stage two thickener overflow was combined with primary filtrate and spent wash solution, then fed into the stage one leach tank along with damp (9% moisture) concentrate (Table 21). Stage one thickener overflow was continuously withdrawn from the system as was washed leach residue cake from stage two. For every kilogram of concentrate (dry basis) feeding into the stage one leach tank, 10.6 kg of phosphoric acid was fed into the first stage two leach tank. The circuit performance is summarised in Table 22.

Table 20: Feed acid composition (g/L or mg/L)

Test	LRE	MRE	HRE	Y	TRE	Al	P	S	Ca	Fe	Th	U
	g/L	mg/L	mg/L	mg/L	g/L	g/L	g/L	g/L	g/L	g/L	g/L	g/L
34	-	-	-	-	-	5.7	212	2	6.3	7.2	-	-

Table 21: Feed concentrate composition (% w/w or g/t)

Test	LRE	MRE	HRE	Y	TRE	Al	P	S	Ca	Fe	Th	U
	%	%	g/t	g/t	%	%	%	%	%	%	%	g/t
34	5.6	0.24	413	835	5.9	1.5	12.4	0.2	29.6	1.3	0.46	422

Table 22: Pre-leach residue composition (% w/w or g/t)

Test	LRE	MRE	HRE	Y	TRE	Al	P	S	Ca	Fe	Th	U
	%	%	g/t	g/t	%	g/t	%	%	%	g/t	%	g/t
34	11.2	0.42	663	1280	11.7	3.8	6.5	1.9	12.5	3.0	0.97	852

Rare earth recovery

[0070] Rare earth recovery tests were conducted by heating a measured quantity of pre-leach solution (rare earth recovery feed solution) to boiling in a suitable well agitated baffled vessel fitted with a reflux condenser. The resulting mixture was maintained under a continuous state of boiling for 120 minutes, then vacuum filtered. The filter cake was then washed thoroughly with DI water to remove entrained solution prior to drying.

[0071] Five rare earth recovery tests were conducted to evaluate the influence of variability in the feed solution composition (Table 23) on the performance of rare earth recovery. The results are summarised in Tables 24 and 25.

Table 23: Feed solution composition (% w/w or g/t)

Test	LRE	MRE	HRE	Y	TRE	Mg	Al	P	Ca	Fe	Th	U
	g/L	mg/L	mg/L	mg/L	g/L	g/L	g/L	g/L	g/L	g/L	mg/L	mg/L
35	2.11	112	23	42	2.28	3.83	3.58	192	36.5	3.44	139	14
36	1.95	103	21	38	2.11	7.45	7.16	196	33.2	6.73	138	14
37	1.74	88	18	33	1.88	14.1	7.20	182	29.5	6.70	114	12
38	1.84	95	20	36	1.99	7.40	10.9	186	31.5	6.90	129	12
39	1.91	105	22	38	2.07	7.09	7.00	182	32.8	3.30	141	14

Table 24: Precipitate composition (% w/w or g/t)

Test	LRE	MRE	HRE	Y	TRE	Mg	Al	P	Ca	Fe	Th	U
	%	%	g/t	g/t	%	g/t	%	%	%	%	%	g/t
35	31.2	1.05	703	645	32.4	< 60	0.13	11.7	4.56	0.34	2.97	24
36	25.6	0.74	499	469	26.4	< 60	0.17	9.16	3.42	0.48	2.44	8.0
37	25.3	0.77	562	532	26.2	< 60	0.16	9.21	3.37	0.70	2.33	8.9
38	24.1	0.66	455	411	24.8	< 60	0.19	8.82	3.22	0.56	2.29	11
39	25.7	0.75	530	500	26.5	< 60	0.19	9.08	3.47	0.27	2.52	8.8

Table 25: Precipitation extent (%)

Test	LRE	MRE	HRE	Y	TRE	Mg	Al	P	Ca	Fe	Th	U
35	80.1	52.1	22.6	7.6	76.9	-	0.18	0.30	0.61	0.49	91.8	0.82
36	71.2	42.2	16.9	6.4	68.1	-	0.12	0.24	0.52	0.37	80.0	0.30
37	81.1	47.1	17.8	8.0	77.5	-	0.11	0.25	0.56	0.51	85.4	0.38
38	68.6	35.2	11.5	5.6	65.2	-	0.08	0.23	0.50	0.39	76.0	0.43
39	73.6	42.6	17.1	6.8	70.1	-	0.14	0.26	0.54	0.41	83.1	0.33

Phosphoric Acid Regeneration

[0072] A continuous phosphoric acid regeneration circuit test was conducted (Test 40). The circuit featured a single 55 minute residence time precipitation tank (Tank 1) operated at 44 °C, followed by a 78 minute stabilisation tank (Tank 2) and batch vacuum filtration, which was supported by duty standby filter feed tanks and was operated with counter current washing. Recovery solution was fed into the precipitation tank along with mixed acid (Table 26). The regeneration performance is summarised in Tables 27 and 29.

Table 26: Feed solution composition (g/L or mg/L)

Solution	LRE	MRE	HRE	Y	TRE	Al	P	S	Ca	Fe	Th	U
	mg/L	mg/L	mg/L	mg/L	mg/L	g/L	g/L	g/L	g/L	g/L	mg/L	mg/L
Recovery	570	94	40	116	704	4.87	184	0.82	27.0	5.42	26	53
Mixed	-	-	-	-	-	3.2	84	379	-	3.2	-	-

Table 27: Precipitate composition (% w/w or g/t)

Tank	LRE	MRE	HRE	Y	TRE	Al	P	S	Ca	Fe	Th	U
	g/t	g/t	g/t	g/t	g/t	g/t	%	%	%	g/t	g/t	g/t
1	1134	85	24	52	1244	1852	1.79	19.2	25.4	420	31	2.2
2	1082	86	24	54	1192	1799	1.68	19.2	25.3	420	31	1.9

Table 28: Regenerated solution composition (g/L or mg/L)

Tank	LRE	MRE	HRE	Y	TRE	Al	P	S	Ca	Fe	Th	U
	mg/L	mg/L	mg/L	mg/L	mg/L	g/L	g/L	g/L	g/L	g/L	mg/L	mg/L
1	436	83	38	105	558	4.75	19.4	2.22	3.91	5.88	26.5	53.1
2	461	86	39	114	586	4.63	19.3	1.66	3.82	5.91	27.2	53.8

Table 29: Overall precipitation extent (%)

Tank	LRE	MRE	HRE	Y	TRE	Al	P	S	Ca	Fe	Th	U
1	21.0	9.5	6.0	4.8	18.5	3.8	0.9	89.8	86.9	0.7	10.8	0.4
2	18.0	8.5	5.5	4.2	16.0	3.5	0.8	91.5	86.1	0.7	9.5	0.3

Acid Bake and Water Leach

[0073] Acid bake water leach tests were conducted by contacting a measured quantity of sulphuric acid with a measured quantity of pre-leach residue with thorough mixing in a suitable dish. The resulting mixture was placed in a furnace and raised to 250 °C over a period of up to 50 minutes, then held at 250 °C for a period of 30 minutes, withdrawn from furnace and allowed to cool. The cool sulphated material was then added to a measured quantity of 5 °C DI water, agitated for 10 minutes, then vacuum filtered. The filter cake was then washed thoroughly with DI water to remove entrained solution prior to drying.

[0074] Six acid bake water leach tests (Tests 41 to 46) were conducted to evaluate the influence of variability in the feed pre-leach residue composition (Table 30) on the performance of acid bake water leach. Each test was conducted using an acid to residue contact ratio of 1600 kg of H₂SO₄ per tonne of leach residue, and 2.5 g of DI per gram of pre-leach residue. The results are summarised in Tables 31 to 33.

Table 30: Feed pre-leach residue composition (% w/w or g/t)

Test	LRE	MRE	HRE	Y	TRE	Al	P	S	Ca	Fe	Th	U
	%	%	g/t	%	%	%	%	%	%	%	%	g/t
41	11.2	0.40	642	0.13	11.7	4.45	7.16	0.64	12.5	3.64	0.98	814
42	10.1	0.33	510	0.10	10.6	3.99	6.33	0.08	14.0	6.20	0.99	729
43	4.15	0.15	229	0.05	4.36	3.69	5.67	0.07	17.0	2.40	0.46	211
44	8.44	0.29	475	0.09	8.86	6.56	8.07	0.05	11.8	0.80	0.58	577
45	18.5	0.65	891	0.19	19.4	0.36	13.9	0.13	22.2	1.28	3.33	1250
46	12.5	0.44	706	0.14	13.1	9.66	6.46	0.02	2.29	1.85	1.42	839

Table 31: Water leach solution composition (g/L or mg/L)

Test	LRE	MRE	HRE	Y	TRE	Al	P	S	Ca	Fe	Th	U
	g/L	g/L	mg/L	mg/L	g/L	g/L	g/L	g/L	g/L	g/L	g/L	mg/L
41	34.9	1.24	170	308	36.7	1.79	22.7	104	0.58	3.08	2.79	280
42	28.0	0.86	108	193	29.2	1.56	18.7	108	0.86	7.35	2.50	219
43	10.0	0.32	34	65	10.4	0.53	16.7	98.6	1.30	0.20	1.06	66
44	25.3	0.81	97	183	26.4	0.87	23.3	92.9	1.46	0.16	1.56	198
45	52.1	1.71	207	372	52.1	0.95	38.7	86.0	0.61	3.48	4.68	374
46	42.5	1.49	220	382	42.5	0.58	17.9	96.4	1.37	0.27	4.35	315

Table 32: Water leach residue composition (% w/w or g/t)

Test	LRE	MRE	HRE	Y	TRE	Al	P	S	Ca	Fe	Th	U
	%	g/t	g/t	g/t	%	%	%	%	%	%	g/t	g/t
41	0.26	264	118	200	0.32	3.93	0.54	13.8	10.6	2.44	251	16.5
42	0.29	193	83	153	0.34	4.07	0.36	8.89	12.2	3.63	141	21.6
43	0.18	152	62	116	0.21	3.55	0.23	9.45	12.4	2.10	480	12.4

44	0.10	139	62	109	0.13	5.56	0.92	14.3	5.34	0.66	267	8.6
45	0.68	897	261	433	0.84	0.35	0.34	21.3	25.9	0.26	4660	24.9
46	0.12	73	56	110	0.14	7.47	1.15	14.7	4.15	1.35	609	14.6

Table 33: Dissolution extent (%)

Test	LRE	MRE	HRE	Y	TRE	Al	P	S ^[1]	Ca	Fe	Th	U
41	98.0	94.5	84.1	85.0	97.7	1.4	93.9	25.5	1.5	31.7	97.6	98.4
42	97.9	95.5	86.3	85.8	97.7	15.5	96.2	14.5	2.2	49.3	98.8	98.0
43	95.5	89.0	68.1	68.3	94.9	5.4	96.5	19.9	2.8	3.5	89.4	95.3
44	98.5	94.0	80.9	82.0	98.2	4.1	87.4	36.0	3.8	6.2	94.1	98.4
45	97.4	90.3	79.4	80.7	96.9	56.9	98.2	33.5	1.0	86.7	83.0	98.6
46	98.8	97.8	89.7	88.5	98.6	1.7	77.4	40.8	16.8	4.2	94.0	97.9

[1] deportment from sulphuric acid to water leach residue for S

Rare earth sulphate dissolution

[0075] Rare earth sulphate dissolution tests are typically conducted by contacting a measured quantity of dry rare earth sulphate precipitate with a measured quantity of DI water with thorough mixing in a suitable well agitated baffled vessel, at 40 °C for a period of 120 minutes, then vacuum filtered. The filter cake was then washed thoroughly with DI water to remove entrained solution prior to drying.

[0076] Five rare earth sulphate dissolution tests (Tests 47 to 51) were conducted to evaluate the influence of variability in the feed composition (Table 34) on the performance of dissolution. Each test was conducted using a water to feed solids contact ratio of 13 grams of DI water per gram of feed solid. Test 47 was operated with a 60 minute dissolution at 22 °C, while tests 48 to 51 were operated with a 120 minute dissolution at 40 °C. The results are summarised in Tables 35 to 37.

Table 34: Feed rare earth sulphate composition (% w/w or g/t)

Test	LRE	MRE	HRE	Y	TRE	Al	P	S	Ca	Fe	Th	U
	%	%	g/t	g/t	%	g/t	%	%	%	g/t	%	g/t
47	35.2	1.05	833	1363	36.5	9185	3.88	12.2	1.97	6902	2.51	123
48	40.0	1.18	712	1050	41.4	< 53	0.22	14.7	0.32	560	0.61	1.4
49	43.4	1.28	999	1680	44.9	212	0.24	14.9	0.51	769	1.47	3.7
50	41.2	0.97	898	1520	42.4	< 53	0.23	14.7	0.17	490	1.88	2.4
51	40.3	1.21	611	757	41.6	476	0.23	14.1	0.41	629	0.76	1.6

Table 35: Dissolution solution composition (g/L or mg/L)

Test	LRE	MRE	HRE	Y	TRE	Al	P	S	Ca	Fe	Th	U
	g/L	mg/L	mg/L	mg/L	g/L	mg/L	mg/L	g/L	mg/L	mg/L	mg/L	mg/L
47	11.4	401	43	68	11.9	500	2950	6.28	690	400	4.8	3.3
48	34.5	1120	92	78	35.8	190	5	14.3	223	10	103	0.15
49	29.6	1084	94	119	30.9	20	< 3	12.1	293	20	286	0.38
50	34.6	843	91	122	35.6	< 10	4	12.8	239	< 10	345	0.17
51	27.2	875	70	72	28.2	< 10	< 3	10.1	166	10	110	0.19

Table 36: Dissolution residue composition (% w/w or g/t)

Test	LRE	MRE	HRE	Y	TRE	Al	P	S	Ca	Fe	Th	U
	%	%	g/t	g/t	%	g/t	%	%	g/t	g/t	%	g/t
47	35.2	0.91	471	536	36.2	5716	8.03	7.53	19900	14618	4.97	145
48	36.9	0.86	180	117	37.8	1799	10.2	0.35	< 72	5735	23.3	3.8
49	22.5	0.53	168	142	23.1	265	7.77	8.01	1001	5106	39.1	3.7
50	5.01	0.12	51	41	5.13	< 53	8.25	2.82	< 71	5456	51.0	4.1
51	30.8	0.64	105	46	31.4	318	8.65	4.13	786	5664	21.8	3.7

Table 37: Dissolution extent (%)

Test	LRE	MRE	HRE	Y	TRE	Al	P	S	Ca	Fe	Th	U
47	53.5	59.5	73.7	81.7	53.8	71.0	3.5	71.3	53.0	1.3	7.6	45.0
48	97.8	98.2	99.4	99.7	97.8	-	2.7	99.9	82.2	21.2	6.2	93.2
49	98.7	99.0	99.6	99.8	98.7	96.9	-	98.7	99.5	32.3	34.1	97.5
50	99.9	99.9	99.9	100	99.9	-	2.0	99.8	-	-	73.1	98.3
51	98.2	98.8	99.6	99.9	98.2	98.4	-	99.3	99.6	20.9	32.6	94.5

Rare Earth Purification

[0077] Rare earth purification tests (Tests 52 and 53) were conducted by dosing magnesia, to a pH 5 endpoint target, to a measured quantity of impure rare earth sulphate solution at 40 °C in a suitable well agitated baffled vessel with online pH measurement. The resulting mixture was mixed for a period of 30 minutes following magnesia addition to allow it to stabilise, then vacuum filtered. The filter cake was then washed thoroughly with DI water to remove entrained solution prior to drying.

[0078] Two rare earth purification tests were conducted to evaluate the influence of variability in the source magnesia (Table 38) on the performance of rare earth purification from a common feed solution (Table 39). The results are summarised in Tables 40 to 42. In both tests (52 and 53), 0.16 kg of MgO was dosed per tonne of feed solution. There was 97.3% utilisation of magnesia in Test 52, and a 91.1% utilisation of magnesia in Test 53.

Table 38: Magnesia composition (% w/w or g/t)

Test	LRE	MRE	HRE	TRE	Mg	Al	P	S	Ca	Fe	Th	U
	g/t	g/t	g/t	g/t	%	%	g/t	g/t	%	%	g/t	g/t
52	28	9.8	3.7	49	39.9	0.09	22	80	2.42	0.18	< 1	0.15
53	26	8.6	3.8	46	38.3	0.05	< 4	40	0.51	0.06	5	0.09

Table 39: Feed solution composition (g/L or mg/L)

Test	LRE	MRE	HRE	TRE	Mg	Al	P	S	Ca	Fe	Th	U
	g/L	mg/L	mg/L	g/L	mg/L	mg/L	mg/L	g/L	mg/L	mg/L	mg/L	mg/L
52 & 53	20.2	725	48	21.1	< 2	< 10	14	7.64	88	< 1	113	0.76

Table 40: Precipitate composition (% w/w or g/t)

Test	LRE	MRE	HRE	TRE	Mg	Al	P	S	Ca	Fe	Th	U
	%	%	g/t	%	%	%	g/t	%	%	%	%	g/t
52	30.1	2.38	1533	32.7	0.61	1.36	882	7.33	0.21	2.06	18.5	17.2
53	24.5	1.74	1030	26.4	2.85	1.83	1157	6.05	0.10	2.67	22.7	17.2

Table 41: Purified rare earth sulphate solution composition (g/L or mg/L)

Test	LRE	MRE	HRE	TRE	Mg	Al	P	S	Ca	Fe	Th	U
	g/L	mg/L	mg/L	g/L	mg/L	mg/L	mg/L	g/L	mg/L	mg/L	mg/L	mg/L
52	20.1	704	45	20.9	79	< 10	11	8.48	92	< 1	0.56	0.45
53	19.8	722	45	20.7	65	< 10	< 3	8.29	89	< 1	1.74	0.13

Table 42: Precipitation extent (%)

Test	LRE	MRE	HRE	TRE	Mg	Al	P	S	Ca	Fe	Th	U
52	0.44	0.97	0.95	0.46	-	-	1.9	0.28	0.67	-	99.5	41.2
53	0.23	0.46	0.42	0.24	-	-	1.6	0.15	0.22	-	98.5	82.9

RE Hydroxide precipitation

The influence of reagent

[0079] Rare earth hydroxide precipitation tests (Tests 54 to 56) were conducted by contacting a measured quantity of magnesia or sodium hydroxide to a measured quantity of purified rare earth sulphate solution at 55 °C in a suitable well agitated baffled vessel. The resulting mixture was mixed for a period of 30 minutes following each dose of reagent addition to allow it to stabilise, then subsample collected, and vacuum filtered. Subsample filter cake was then washed thoroughly with DI water to remove entrained solution prior to drying. For each test, a range of subsamples were collected to cover a range of reagent doses. Following the final precipitation subsample, a measured quantity of hydrogen peroxide was added to the remaining slurry. The resulting mixture was mixed for a period of 30 minutes to allow it to stabilise, then vacuum filtered.

[0080] Two of the rare earth hydroxide precipitation tests (Test 54 and 55) were conducted to evaluate the influence of variability in the source of magnesia (Table 43) on the performance of rare earth hydroxide precipitation, while the third test (Test 56) evaluated the use of sodium hydroxide. All three tests were based on a common feed solution (Table 44). Reagent dosing is summarised in Table 45. The results are summarised in Tables 46 and 47. From the results it can be seen that the use of magnesia results in significantly increased impurities in the resultant precipitate relative to precipitation using sodium hydroxide. In addition, increased dose rates result in reduced overall deportment of sulphate to rare earth hydroxide precipitate.

Table 43: Magnesia composition (% w/w or g/t)

Test	LRE	MRE	HRE	TRE	Mg	Al	P	S	Ca	Fe	Th	U
	g/t	g/t	g/t	g/t	%	%	g/t	g/t	%	%	g/t	g/t
54	28	9.8	3.7	49	39.9	0.09	22	80	2.42	0.18	< 1	0.15
55	26	8.6	3.8	46	38.3	0.05	< 4	40	0.51	0.06	5	0.09

Table 44: Feed solution composition (g/L or mg/L)

Test	LRE	MRE	HRE	TRE	Mg	Al	P	S	Ca	Fe	Th	U
	g/L	mg/L	mg/L	g/L	mg/L	mg/L	mg/L	g/L	mg/L	mg/L	mg/L	mg/L
54 to 56	20.5	760	48	21.4	72	< 10	< 3	7.49	90	< 1	0.73	0.21

Table 45: Reagent Addition^[1]

Sample	A	B	C	D	E
54	8.6	9.1	9.6	10.2	125
55	8.6	9.0	9.6	10.1	126
56	16.9	17.9	19.0	20.1	126

[1] Subsamples A through D correspond to periods of magnesia (Tests 54 and 55) or sodium hydroxide (Test 56) addition, where dosing is in the units kg Magnesia or NaOH per t of feed. Subsample E corresponds to a period of hydrogen peroxide dosing with reagent addition expressed as a percentage of stoichiometry.

Table 46: Precipitate composition (% w/w or g/t)

Test	LRE	MRE	HRE	TRE	Mg	Al	P	S	Ca	Fe	Th	U
	%	%	g/t	%	%	g/t	g/t	%	%	g/t	g/t	g/t
54A	51.9	1.52	713	53.6	2.80	318	109	6.57	0.17	769	109	1.25
54B	53.9	1.60	744	55.7	2.98	318	92	5.73	0.16	839	78	1.48
54C	57.0	1.67	783	58.9	2.46	265	92	4.25	0.21	909	82	1.33
54D	56.6	1.65	777	58.4	2.76	265	83	3.45	0.14	909	84	1.34
54E	58.6	1.75	826	60.5	2.48	529	92	3.04	0.17	1049	87	1.44
55A	51.4	1.54	733	53.1	2.35	212	92	6.77	0.06	489	74	1.16
55B	50.7	1.51	715	52.4	2.36	159	87	5.81	0.15	489	75	1.17
55C	50.6	1.50	717	52.3	2.40	159	87	5.17	0.20	489	74	1.21
55D	50.1	1.50	710	51.7	2.81	159	83	4.85	0.21	559	73	1.19
55E	52.7	1.57	762	54.4	2.53	212	92	4.41	0.20	629	79	1.21

Test	LRE	MRE	HRE	TRE	Mg	Al	P	S	Ca	Fe	Th	U
56A	58.8	1.73	844	60.8	0.23	< 53	83	3.10	0.34	489	86	1.33
56B	63.8	1.89	934	65.9	0.23	< 53	96	2.60	0.41	489	97	1.48
56C	63.1	1.88	886	65.2	0.22	< 53	92	1.60	0.46	489	93	1.48
56D	63.9	1.90	907	66.0	0.22	< 53	74	1.17	0.44	420	96	1.55
56E	67.8	2.04	968	70.1	0.23	< 53	87	0.46	0.51	489	97	2.20

Table 47: Precipitation extent (%)

Test	LRE	MRE	HRE	TRE	Mg	Al	P	S	Ca	Fe	Th	U
54A	99.4	99.3	99.2	99.4	-	-	-	38.4	22.5	-	90.3	97
54B	99.9	99.9	99.8	99.9	-	-	-	33.0	20.7	-	90.3	> 97
54C	100	99.9	100	100	-	-	-	23.3	22.3	-	92.2	> 97
54D	99.9	99.9	99.9	99.9	-	-	-	17.9	15.2	-	93.8	> 97
54E	99.9	99.9	100	99.9	-	-	-	14.6	17.4	-	94.1	> 97
55A	99.5	100	100	99.5	-	-	-	36.5	15.4	-	93.5	> 97
55B	99.9	99.9	99.9	99.9	-	-	-	30.1	36.8	-	94.9	> 97
55C	100	99.8	99.5	99.9	-	-	-	31.8	48.1	-	90.5	> 97
55D	99.9	99.9	99.9	99.9	-	-	-	24.9	47.6	-	87.9	> 97
55E	99.9	99.9	99.9	99.9	-	-	-	22.4	48.0	-	92.8	> 97
56A	99.8	99.8	99.7	99.8	-	-	-	13.5	86.5	-	93.3	> 96
56B	99.9	99.9	99.9	99.9	-	-	-	11.3	93.7	-	94.4	> 96
56C	99.9	99.8	99.9	99.9	-	-	-	6.6	> 97	-	95.1	> 95
56D	99.8	99.8	99.8	99.8	-	-	-	4.6	> 97	-	95.3	> 95
56E	99.9	99.9	99.9	99.9	-	-	-	1.7	> 97	-	95.8	> 95

Two stage rare earth hydroxide production

[0081] A rare earth hydroxide precipitation test (Test 57) was conducted by contacting a measured quantity sodium hydroxide (97% of stoichiometry) to a

measured quantity of purified rare earth sulphate solution (Table 48) at 55 °C in a suitable well agitated baffled vessel. The resulting mixture was mixed for a period of 30 minutes to allow it to stabilise, then a measured quantity of hydrogen peroxide (117% of stoichiometry) was added. The resulting mixture was mixed for a period of 30 minutes to allow it to stabilise, then vacuum filtered.

[0082] For the second stage, the unwashed cake from the first stage was repulped in DI water along with a measured quantity of sodium hydroxide (same mass as first stage). The mixture was agitated for 60 minutes at 55 °C then vacuum filtered. The resultant cake was washed.

[0083] The results are summarised in Tables 49 to 50.

Table 48: Feed solution composition (g/L or mg/L)

Test	LRE	MRE	HRE	TRE	Mg	Al	P	S	Ca	Fe	Th	U
	g/L	mg/L	mg/L	g/L	mg/L	mg/L	mg/L	g/L	mg/L	mg/L	mg/L	mg/L
57	20.5	632	39	21.2	80	< 10	< 3	8.12	283	< 10	1.2	0.05

Table 49: Precipitate composition (% w/w or g/t)

Stage	LRE	MRE	HRE	TRE	Mg	Al	P	S	Ca	Fe	Th	U
	%	%	g/t	%	%	g/t	g/t	%	%	g/t	g/t	g/t
1	64.6	1.57	748	66.4	0.29	< 53	175	2.38	0.33	350	69	2.09
2	66.9	1.69	802	68.8	0.34	< 53	87	0.30	0.46	280	73	2.36

Table 50: Precipitation (Stage 1) or dissolution (Stage 2) extent (%)

Stage	LRE	MRE	HRE	TRE	Mg	Al	P	S	Ca	Fe	Th	U
1	99.9	99.8	99.9	99.9	97.0	-	-	10.0	75.6	-	97.9	>80
2	0	0	0	0	0	0	0	93	0	0	5	21

Selective Dissolution

The influence of rare earth concentration

[0084] A series of four two stage rare earth hydroxide dissolution tests (Tests 58 to 61) were conducted at 70 °C in a suitable well agitated baffled vessel with online pH measurement. Each test starts by simulating the second stage by dosing with a measured portion of 10% w/w hydrochloric acid to a measured portion of rare earth hydroxide cake (Table 51) that has been repulped in DI water (Test 58) or rare earth chloride solution (Tests 59 to 61), followed by a 30 minute period of stabilisation. Typically, this results in a slurry pH of around 1.2 to 2.2. Each test then concludes with the second stage by adding a measured quantity of rare earth hydroxide cake (typically 1.5 times that used to initiate the test), observing a 30 minute period of stabilisation, then dosing with a measured portion of 10% w/w hydrochloric acid, followed by a 30 minute period of stabilisation. Typically, this results in a slurry pH of around 3 to 4. The test is then concluded with vacuum filtration, followed by cake washing.

[0085] Tests 59 to 61 were initiated using rare earth chloride solution from test 58, with 2.8, 5.3, and 8.4 g of rare earth chloride solution added to tests 59 to 61 respectively per gram of rare earth hydroxide consumed by each test. The results are summarised in Tables 52 to 53.

Table 51: Feed Solid composition (% w/w or g/t)

Test	LRE	MRE	HRE	TRE	Mg	Al	P	S	Ca	Fe	Th	U
	%	%	g/t	%	%	g/t	g/t	%	%	g/t	g/t	g/t
58 to 61	66.9	1.69	802	68.8	0.34	< 53	87	0.30	0.46	280	73	2.36

Table 52: Final dissolution solution composition (g/L or mg/L)

Test	LRE	MRE	HRE	Ce	Mg	Al	P	S	Ca	Fe	Th	U
	g/L	g/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
58	51.2	2.16	110	< 1	482	30	< 3	< 1	1330	< 10	0.14	< 0.01
59	137	5.14	261	< 1	1220	60	< 3	< 1	3620	< 10	0.05	< 0.01
60	259	10.0	501	< 1	2180	110	< 3	< 1	6820	< 10	0.04	< 0.01
61	366	14.0	704	< 1	2970	150	< 3	40	9400	< 10	0.03	< 0.01

Table 53: Overall dissolution extent (%)

Test	La	Ce	Pr	Nd	MRE	HRE	Y	Mg	Al	Ca	Th
58	94.8	< 0.0021	82.0	78.3	69.1	60.6	67.6	94.2	-	98.7	0.9
59	92.5	< 0.0015	73.1	67.1	49.0	39.9	39.0	90.6	-	97.3	0
60	94.8	< 0.0013	79.2	74.6	58.6	46.6	45.3	89.9	-	98.5	0
61	95.2	< 0.0012	80.4	75.1	57.4	43.4	43.7	87.6	-	98.5	0

Two stage selective dissolution

[0086] A two stage rare earth hydroxide dissolution test (Test 62) was conducted at 70 °C in a suitable well agitated baffled vessel with online pH measurement. The test was initiated by repulping 60% of the rare earth hydroxide cake (Table 54) in de-ionised water followed by the controlled dosing of 10% w/w hydrochloric acid to online pH targets of pH 2 (sample 1), then pH 1 (sample 2). At pH 1, all of the rare earth hydroxide precipitate had been dissolved. The remaining 40% of the rare earth hydroxide cake was then added and the mixture allowed to stabilise under agitation for 30 minutes (sample 3). Controlled acid addition was then resumed to pH 3 (sample 4), pH 2 (sample 5), and pH 1 (sample 6). This time the rare earth hydroxide cake did not completely dissolve. The final slurry was allowed to agitate for a further 50 minutes prior to collection of the final sample (sample 7). Following each period of acid dosing and achievement of an on-line pH target, the resultant mixture was allowed to mix for at least 15 minutes prior to sample collection. Subsamples were vacuum filtered, followed by cake washing.

[0087] The results are summarised in Tables 55 to 57. From the results, despite completely dissolving all the cerium in rare earth hydroxide by sample 2, the addition of additional rare earth hydroxide drove a reprecipitation such that by sample 4 (targeting pH 3, achieving pH 3.2 after stabilisation) the concentration of cerium in solution was below detection limit. This suggests that the cerium dissolved as cerium IV in this test.

Table 54: Feed Solid composition (% w/w or g/t)

Test	LRE	MRE	HRE	Y	Mg	Al	P	S	Ca	Fe	Th	U
	%	%	g/t	g/t	%	g/t	g/t	%	%	g/t	g/t	g/t
62	68.3	1.81	2163	5290	0.18	159	148	0.32	0.49	420	3.5	1.9

Table 55: Subsample dissolution solution composition (g/L or mg/L)

Sample	La	Ce	Pr	Nd	MRE	HRE	Y	Mg	Al	S	Ca
	g/L	mg/L	g/L	g/L	g/L	mg/L	mg/L	mg/L	mg/L	g/L	mg/L
1	13.8	142	2.58	8.84	1.21	149	364	56	< 20	2	978
2	17.4	32400	3.51	12.1	1.80	228	500	206	< 20	242	1206
3	18.2	20	1.83	5.51	0.28	15	32	78	< 20	< 2	1494
4	22.6	< 2	4.16	14.3	1.86	201	552	90	< 20	10	1592
5	20.8	20	4.20	14.5	1.96	224	538	80	< 20	4	1426
6	26.2	2900	5.51	19.1	2.60	303	760	122	20	24	1784
7	31.2	4940	6.44	22.2	3.17	372	900	130	20	20	2140

Table 56: Subsample solid composition (% w/w or g/t)

Sample	La	Ce	Pr	Nd	MRE	HRE	Y	Mg	Al	S	Ca	Fe
	%	%	%	%	%	g/t	g/t	%	g/t	%	g/t	g/t
1	1.12	63.1	0.89	3.29	0.55	894	1530	0.18	265	0.61	286	699
2	-	-	-	-	-	-	-	-	-	-	-	-
3	3.14	47.7	3.05	11.5	2.23	3021	7090	0.15	265	0.46	572	560
4	0.92	63.2	1.03	3.61	0.69	1194	1560	0.11	423	0.60	214	699
5	0.64	65.0	0.68	2.43	0.46	735	1020	0.10	212	0.61	214	629
6	0.54	66.0	0.54	1.85	0.35	552	752	0.10	1006	0.63	214	1189
7	0.61	68.2	0.56	2.01	0.36	567	842	0.10	265	0.64	214	909

Table 57: Overall dissolution extent (%)

Sample	La	Ce	Pr	Nd	MRE	HRE	Y	Mg	Al	Ca	Th
1	97.2	0.6	88.9	88.2	86.0	82.3	86.9	59.0	-	99.0	16.7
2	100	100	100	100	100	100	100	100	100	100	100
3	88.0	0.053	43.1	37.6	13.8	5.8	5.4	39.5	-	97.1	14.3
4	97.6	< 0.005	87.0	86.7	81.6	73.6	85.4	56.5	-	99.2	11.3
5	98.4	0.057	92.0	91.7	88.9	85.0	90.7	59.2	-	99.2	11.9
6	99.4	13.9	97.4	97.4	96.5	95.3	97.4	81.4	42.3	99.7	41.5
7	99.4	19.6	97.5	97.4	96.7	95.7	97.3	81.0	71.7	99.7	39.7

[0088] A person skilled in the art will understand that there may be variations and modifications other than those specifically described. It is to be understood that the invention includes all such variations and modifications. The invention also includes all steps, features, compositions and compounds referred to, or indicated in this specification, individually or collectively, and any and all combinations of any two or more of the steps or features.

The claims defining the invention are as follows:

1. A method of processing a rare earth sulphate solution, the method including the steps of:
 - a) contacting the rare earth sulphate solution with sodium hydroxide to precipitate rare earths as rare earth hydroxide, including the addition of an oxidant to oxidise cerium contained in the rare earth hydroxide precipitate; and
 - b) selectively leaching the rare earth hydroxide precipitate with hydrochloric acid to form a rare earth chloride solution and a residue.
2. The processing method of claim 1, wherein the precipitation occurs in a two-stage counter-current process, including a precipitation stage and refining stage, wherein the rare earth sulphate solution feeds into the precipitation stage with spent solution from the refining stage, to precipitate rare earth hydroxide containing sulphate.
3. The processing method of claim 2, wherein the sulphate containing rare earth hydroxide is subsequently converted to clean rare earth hydroxide in the refining stage with the addition of fresh sodium hydroxide.
4. The processing method of claim 2 or claim 3, wherein the oxidant is hydrogen peroxide and/or sodium hypochlorite, which is added to the precipitation and/or refining stages following sodium hydroxide addition.
5. The processing method of any one of claims 2 to 4, wherein both the precipitation and the refining stage operate at a temperature of 40 to 80°C, and for a time of about 30 to 60 minutes, with the stoichiometry of sodium hydroxide addition being in the range of 100 to 110%, and with 100 to 130% of stoichiometry dosing of oxidant.
6. The processing method of any one of claims 1 to 5, wherein the rare earth chloride solution produced contains negligible cerium, and the residue produced consists primarily of cerium (IV) hydroxide.

7. The processing method of any one of claims 1 to 6, wherein the selective leaching of rare earth hydroxide precipitate is conducted in two stages, each stage having multiple tanks and each stage using hydrochloric acid diluted to 5 to 15% w/w with leach solution from the first leach stage.
8. The processing method of claim 7, wherein leach solution from the second leach stage is used to re-pulp, leach rare earth hydroxide precipitate, and precipitate cerium (IV) dissolved in the second leach stage, prior to the first leach stage.
9. The processing method of claim 7 or claim 8, wherein the selective leaching occurs at a temperature of 60 to 80 °C, the first leach stage is operated to maximise rare earth dissolution while minimising cerium (IV) dissolution, which is achieved with an endpoint pH of about pH 3 to 4, and the second leach stage is operated to minimise the concentration of non-cerium rare earth elements in the residue.
10. The method of any one of claims 1 to 9, wherein barium chloride is added to the rare earth chloride solution, with sulphuric acid when sulphate levels are low, to remove radium via co-precipitation with barium sulphate to form a purified rare earth chloride solution.
11. The method of claim 10, wherein the purified rare earth chloride solution is concentrated by evaporation.

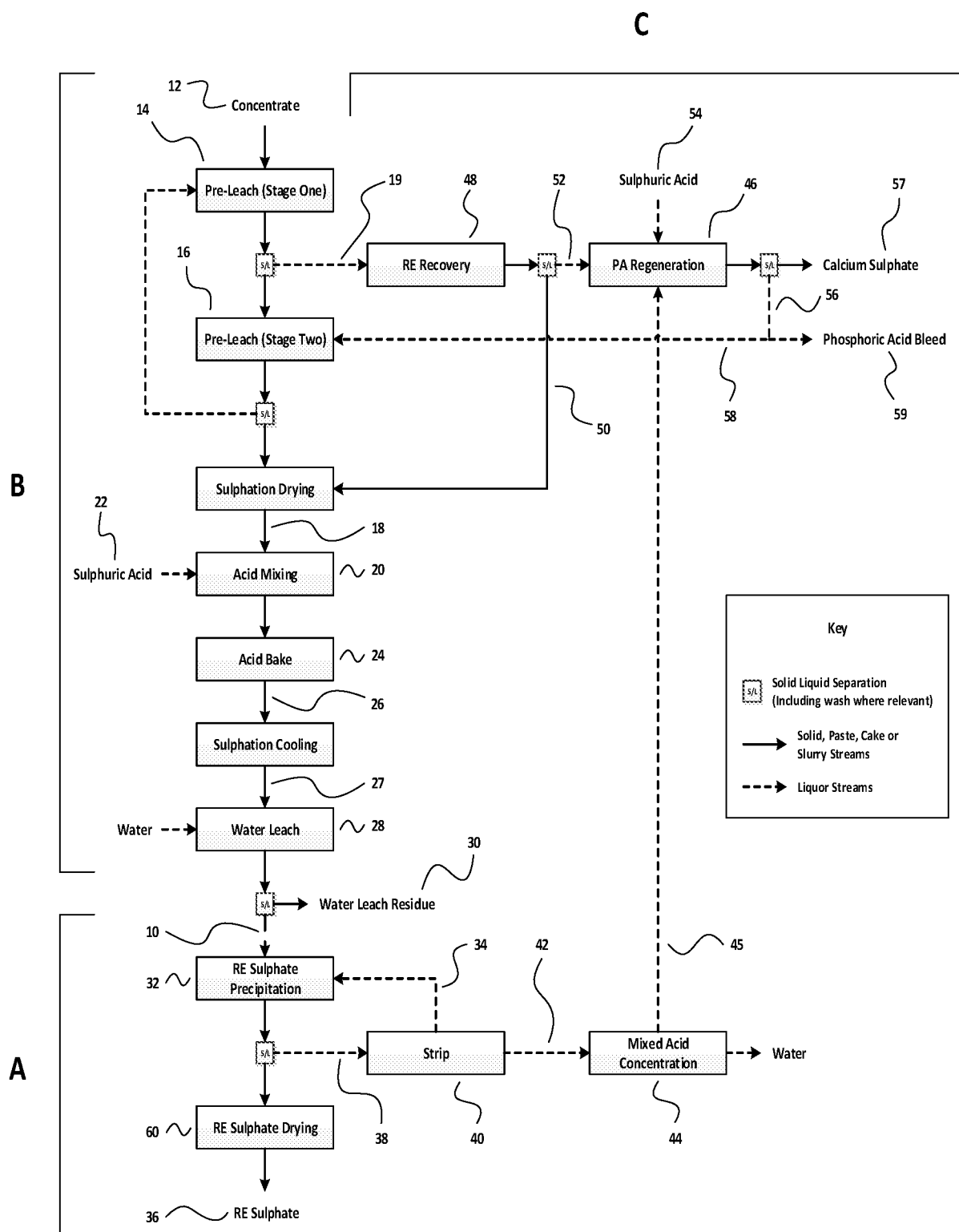


Figure 1

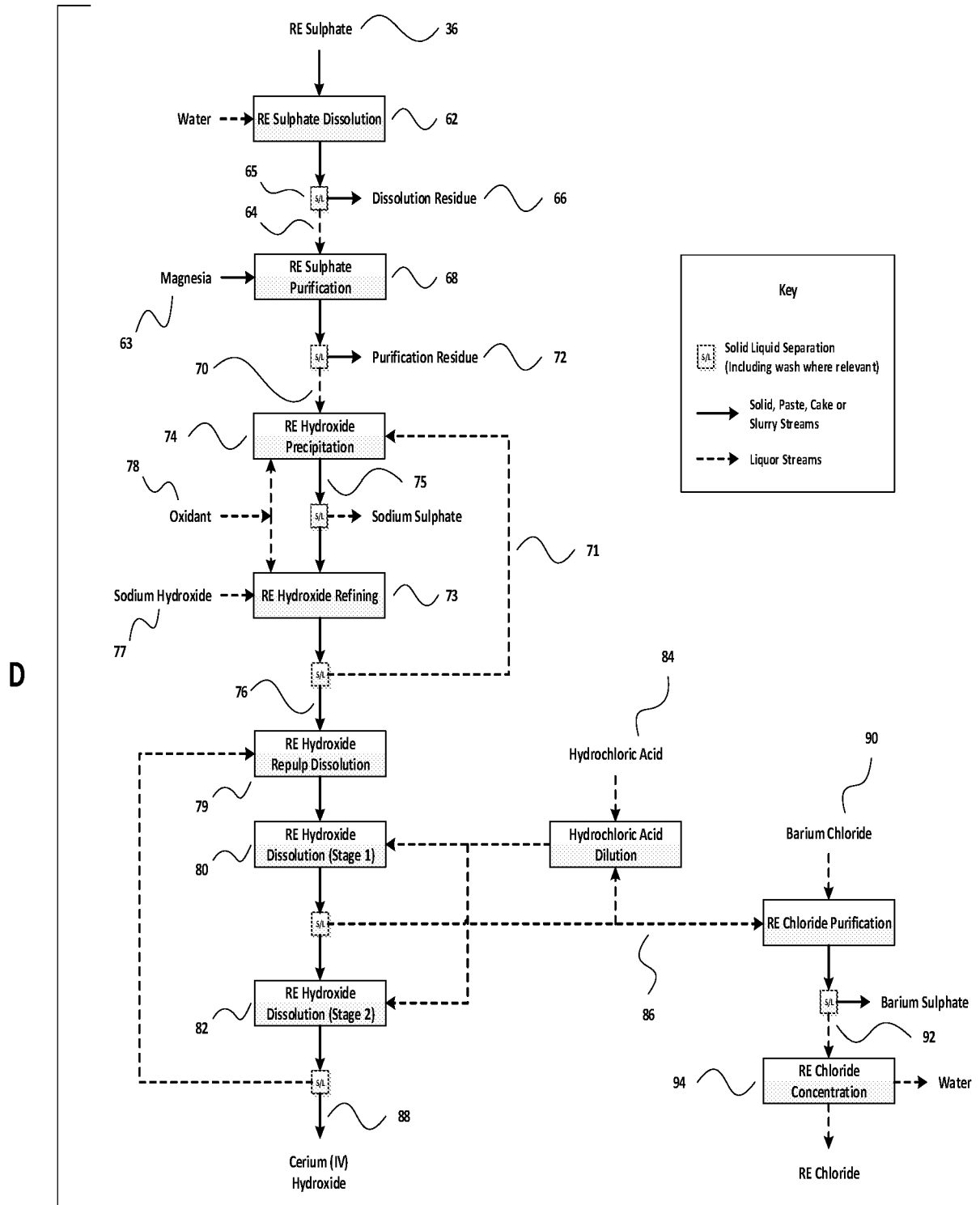


Figure 2

INTERNATIONAL SEARCH REPORT

 International application No.
PCT/AU2019/050403

A. CLASSIFICATION OF SUBJECT MATTER

C22B 59/00 (2006.01) C22B 3/08 (2006.01) C22B 3/04 (2006.01) C01F 17/00 (2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Database: PATENW IPC/CPC Marks: C22B3/04/LOW, C22B59/LOW, C01F17/LOW, C22B3/LOW and Keywords: PRECIPITATION, SULPHATE, NAOH, CERIUM, HCL, OXIDANT, TRIVALENT, TETRAVALENT and like terms

GOOGLE PATENTS searched using a combination of CPC/IPC Marks: C22B3/04, C22B59 and keywords: SULPHATE, CERIUM, RARE EARTH, HCL, NAOH, PRECIPITATION and their like terms

Applicant(s)/Inventor(s) name searched in AUSPAT, ESPACENET and internal databases provided by IP Australia

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	Documents are listed in the continuation of Box C	



Further documents are listed in the continuation of Box C



See patent family annex

* "A"	Special categories of cited documents: document defining the general state of the art which is not considered to be of particular relevance	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E"	earlier application or patent but published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search 27 June 2019	Date of mailing of the international search report 27 June 2019
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA Email address: pct@ipaustalia.gov.au	Authorised officer Thomas Yan AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No. +61262832613

INTERNATIONAL SEARCH REPORT		International application No.
C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		PCT/AU2019/050403
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	AU 2014250661 A1 (ARAFURA RESOURCES LIMITED) 15 October 2015 Figs. 1-3; Paragraphs 53-61, 64, 75-76	1-11
X	KR 10-1766788 B1 (NATIONAL INSTITUTE OF ENVIRONMENTAL RESEARCH) 11 August 2017 & Family member US 2018/0195146 A1 used as English Translation Figs. 1; Paragraphs 23-27, 49	1

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INTERNATIONAL SEARCH REPORT Information on patent family members		International application No. PCT/AU2019/050403	
This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.			
Patent Document/s Cited in Search Report		Patent Family Member/s	
Publication Number	Publication Date	Publication Number	Publication Date
AU 2014250661 A1	15 October 2015	AU 2014250661 A1	15 Oct 2015
KR 10-1766788 B1	11 August 2017	KR 101766788 B1	11 Aug 2017
		US 2018195146 A1	12 Jul 2018
End of Annex			
Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001. Form PCT/ISA/210 (Family Annex)(revised January 2019)			