



- (51) **International Patent Classification:**
C07F 5/00 (2006.01) *B01D 11/04* (2006.01)
- (21) **International Application Number:**
PCT/US2017/000040
- (22) **International Filing Date:**
20 July 2017 (20.07.2017)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (30) **Priority Data:**
62/494,101 27 July 2016 (27.07.2016) US
- (71) **Applicant: IOWA STATE UNIVERSITY RESEARCH FOUNDATION, INC.** [US/US]; 1805 Collaboration Place, Suite 2100, Ames, IA 50010 (US).
- (72) **Inventors: MUDRING, Anja-Verena;** 3915 Stone Brooke Circle, Ames, IA 50010 (US). **PRODIUS, Denis;** 301 S. 5th Street-apt. 390, Ames, IA 50010 (US).
- (74) **Agent: TIMMER, Edward, J.;** 526 W. 14th Street - Ste 311, Traverse City, MI 49684 (US).

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))

- (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,

- (54) **Title:** SEPARATING RARE EARTH METAL OXALATES

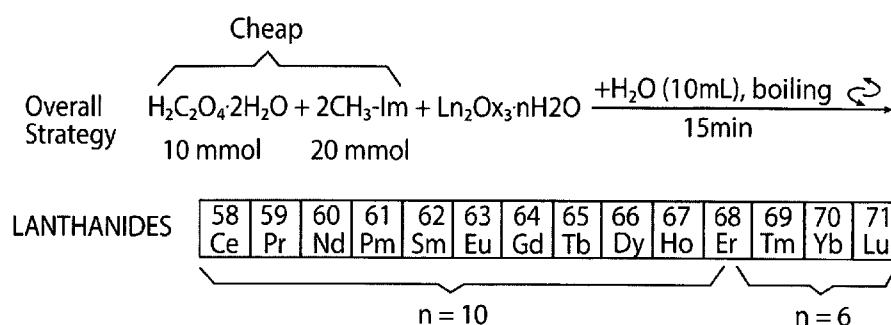


FIG. 1

(57) **Abstract:** A method is provided for separating different rare earth metal oxalates by mixing the different rare earth metal oxalates in an aqueous solution comprising oxalic acid and an organic base so that at least one rare earth metal oxalate is soluble and at least another rare earth metal oxalate is not soluble. The different rare earth metal oxalates that can be separated can include at least one light rare earth metal oxalate and at least one heavy rare earth oxalate, or different heavy rare earth metal oxalates. The separation method can be incorporated as a step in a solvent extraction method that generates rare earth metal oxalates as an intermediate reaction product to simplify extraction processing and lower extraction costs.



SEPARATING RARE EARTH METAL OXALATES

RELATED APPLICATION

[0001] This application claims benefit and priority of U.S. provisional application Serial No. 62/494,101 filed July 27, 2016, the entire disclosure of which is incorporated herein by reference.

CONTRACTUAL ORIGIN OF THE INVENTION

[0002] This invention was made with government support under Grant No. DE-AC02-07CH11358 awarded by the U.S. Department of Energy. The government has certain rights in the invention.

FIELD OF THE INVENTION

[0003] The present invention relates to a method for separating rare earth metal oxalates based on solubility differences in an aqueous solution of oxalic acid and an organic base and to a rare earth metal extraction method embodying the separating step.

BACKGROUND OF THE INVENTION

[0004] The lighter rare earth elements such as lanthanum, cerium, praseodymium, and neodymium are more abundant and concentrated and usually make up about 80%-99% of a total ore deposit. The heavier elements (Gd-Lu), which are actually on average 8-125 times more expensive than the light lanthanides, are rarer but highly demanded.

[0005] Historically separation of lanthanides can be divided into four main groups such as chemical separation, fractional crystallizations, ion-exchange methods and solvent extraction. Apart from initial chemical separation of cerium and repeated fractional crystallization (time-consuming, up to 15000 cycles), nowadays only solvent extraction and ion-exchange methods are used on a commercial scale. Ion-exchange chromatography is not of real commercial importance for large-scale production (disadvantage is that it is a slow process) but for electronic or spectroscopic use ('phosphor grade', 99.999% purity) it is still an indispensable tool.

[0006] Solvent extraction is recognized as an important and main industrial technology for separation and purification of rare-earth elements. Acidic organophosphorous extractants, such as tributyl phosphate or di-2-ethylhexyl phosphoric acid (D2EHPA), are widely used for this purpose. Industrially the rare earths usually were recovered from the leach liquor by solvent extraction with 25% D2EHPA in kerosene, followed by multistage pulling of the rare earths from the organic solution and precipitation with oxalic acid. The final step is calcination and transformation of the rare-earth oxalates into oxides. The disadvantages of this approach are the complexity of the process and large scale use of hazardous chemicals (e.g. organophosphorous compounds). Therefore, there is an economical, ecological and strategic need in the development of new efficient low-cost extractants and extraction systems for separating them as a group or from each other.

SUMMARY OF THE INVENTION

[0007] The present invention provides a selective chemical separation method of rare earth metal oxalates to address this need wherein the method involves mixing different rare earth metal oxalates and an aqueous solution comprising oxalic acid and an organic base wherein at least one rare earth metal oxalate is soluble and at least another rare earth metal oxalate is not soluble in the aqueous solution.

[0008] In an illustrative embodiment of the invention, the different rare earth metal oxalates include at least one light rare earth metal (La-Sm) oxalate and at least one heavy rare earth (Gd-Lu) oxalate that are separated.

[0009] In another illustrative embodiment of the invention, different heavy rare earth metal oxalates are separated.

[0010] In another illustrative embodiment of the invention, the aqueous solution comprises 5 to 95 % oxalic acid and 95 to 5 % organic base, wherein the organic base is selected from the group consisting of organic amines, phosphines or thioesters. A preferred organic base for use in practice of the invention comprises 1-methylimidazole.

[0011] The present invention envisions incorporating the separating method of the invention as a method step in a solvent extraction method that generates rare earth metal oxalates as an intermediate reaction product. The chemical separating step of the invention is employed to separate the different rare earth metal oxalates and simplify and reduce the cost of the overall extraction process.

[0012] Practice of the present invention provides the following advantages:

- 1) Chemical separation of lanthanide oxalates within two groups: La-Sm (low-priced) and Gd-Lu (high-priced).
- 2) Simple and fast: (a) no special equipment or extreme synthetic conditions are required for the extractant preparation; (b) it is a 'one step' separation process which takes a few minutes.
- 3) Environmental Aspects: (a) It is a water-based process (no mineral acids or organic 2nd phase required); (b) The preferred organic base, 1-methylimidazole, is recognized by Sigma-Aldrich Company as a Greener Alternative Product which adheres to one or more of the "12 Principles of Green Chemistry".
- 4) Cost effective: The required materials (oxalic acid and the respective base) as well as the whole process are cheaper compared to the state-of-art solvent extraction with organophosphorus compounds.
- 5) The separation process represents a substantial improvement to known separation technology.

[0013] The present invention will become more readily understood from the following detailed description taken with the drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] Figure 1 is schematic diagram of the overall chemical separation method pursuant to an illustrative embodiment of the invention.

[0015] Figure 2 is graph of solubility distribution, SF, versus lanthanide elements showing their relative solubility values in particular aqueous solutions tested each containing a different organic base. SF(Nd) and SF(Pr) mean the separation factors of the selected lanthanides versus solubility values of neodymium or praseodymium oxalates, respectively, in particular aqueous solutions for the respective organic base.

[0016] Figure 3A is a schematic diagram of a conventional solvent extraction process having four steps.

[0017] Figure 3B is a schematic diagram of a solvent extraction process modified to include step D in accordance with an embodiment of the invention.

DESCRIPTION OF THE INVENTION

[0018] The present invention relates to a selective chemical separation of rare earth oxalates in particular aqueous media into different subgroups involving light rare earth metals and/or heavy rare earth metals.

[0019] For example, one illustrative embodiment of the invention involves chemical separation of one or more light rare earth metal oxalates, such as at least one of La through Sm of the Periodic Table of Elements, and one or more heavy rare earth oxalates, such as at least one of Gd through Lu of the Periodic Table of Elements.

[0020] Another illustrative embodiment of the invention involves separation of different heavy rare earth metal oxalates, such as Gd through Lu of the Periodic Table of Elements.

[0021] Practice of an illustrative embodiment of the invention involves mixing the different rare earth metal oxalates, which can be a main intermediate reaction product of the solvent extraction process, and an aqueous solution comprising oxalic acid and an organic base wherein one or more rare earth metal oxalates is/are soluble and one or more other rare earth metal oxalates is/are not soluble in the aqueous solution.

[0022] The aqueous solution can comprise 5 to 95 mole % oxalic acid and 95 to 5 mole % of organic base, balance being water. The aqueous solution preferably comprises 30 to 40 mole % oxalic acid 60 to 70 mole % of organic base, balance being water. The aqueous solution even more preferably comprises 32 to 34 mole % oxalic acid and 66 to 68 mole % of organic base, balance being water.

[0023] The pH of the aqueous solution typically is maintained in the range of 6 to 8, while the temperature of the aqueous solution typically is maintained in the temperature range of 80 to 100 °C in practice of the embodiments of the invention. The aqueous solution containing the rare earth metal oxalates typically is stirred or otherwise agitated during the separation method.

[0024] The organic base is selected generally from the group consisting of imidazoles, pyridines, methyl amines, benzimidazoles, histidines, phosphazene bases, or other organic bases (e.g. N-containing, P-containing, S-containing organic bases).

[0025] Particular organic bases of interest include 1-methylimidazole, 1-ethylimidazole, methylpyrrolidine, and 1-butylimidazole. A preferred organic base comprises 1-methylimidazole.

[0026] The following Examples are offered to further illustrate practice of the invention without limiting the invention in any way.

[0027] Examples:

In these Examples, water-insoluble rare earth oxalates, which are one of the main intermediate products of the industrial production of lanthanides, are selectively reacted with a mixture of oxalic acid and an organic base (e.g. mim = 1-methylimidazole, eim = 1-ethylimidazole, mpr = 1-methylpyrrolidine), which allows for their separation based on solubility differences in the aqueous phase. Figure 1 illustrates the overall chemical separation method pursuant to an illustrative embodiment of the invention using 1-methylimidazole (mim) as the organic base.

[0028] In a typical one stage bench-scale testing, to a solution of oxalic acid ($\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, 10 mmol, 1.2607 g) and the organic base (20 mmol) in 10 mL of water, a specific amount (up to about 1.6 mmol) of $\text{Ln}_n\text{O}_x \cdot n\text{H}_2\text{O}$ (where O_x = oxalate; $n = 10$ (for La-Er) and 6 (for Er-Lu)) was added. The mixture was stirred for 15min at 100°C (boiling). Each rare earth oxalate was added in drop-wise up to a maximum oxalate amount which could be dissolved in the solution (without precipitation within the 30 minute subsequent to dropwise introduction).

[0029] A solubility distribution (SD) parameter was defined as the concentration of a lanthanide in the aqueous phase. The ratio of solubility distributions (SD) between two components (in this case concentrations of dissolved lanthanide oxalates) is stipulated here as the separation factor (SF_{Ln1}) (eq.1):

$$SF_{Ln1} = C_{Ln}^i / C_{Ln1} \quad (1)$$

where C_{Ln}^i is the concentration of a specific lanthanide oxalate and C_{Ln1} is concentration (solubility value) of the selected as reference, low soluble, lanthanide oxalate (e.g. Nd or Pr oxalate).

[0030] Figure 2 summarizes the solubility distribution (SD) values versus lanthanide elements tested in the manner described above. Figure 2 reveals and demonstrates that light rare earth oxalates (LREOX, La-Sm) were practically insoluble in comparison to the heavy rare earth oxalates (HREOX, Gd-Lu) thus making it possible to transfer exclusively the HREOX to the aqueous phase.

[0031] Figure 2 also reveals that the solubility distribution (SD) values versus the heavy rare earth oxalates (HREOX, Gd-Lu) can be used to separate different heavy rare earth metals based on solubility differences in the aqueous phase. For example, the heavy rare earth metals including at least one of Gd, Tb, and Dy can be separated from at least one of Tm, Yb, and Lu based on solubility differences.

[0032] Referring to Figure 3A, the present invention makes possible to divide different price category lanthanides at the early stages of separation (starting already at STEP 3 instead of STEP 4 of a solvent extraction process, which as a consequence can effectively reduce for suppliers the self-cost of rare earth (La, Ce, Pr, Nd) oxides widely used as component of FCC (Fluid Catalytic Cracking) catalyst in crude petroleum refining (see Example 2).

[0033] For example, in Figure 3A, the starting materials are indicated to be rare earth metal-bearing Monazite sand and concentrated sulfuric acid (98%). In step 1, the sand and sulfuric acid are heated at 120 and 150 °C for several hours. The leach liquor (gray mud) then is mixed with cold water in step 2, and the residue (e.g. sand and

TiO₂, etc.) is allowed to settle out, leaving water-soluble sulfates of rare earth metals. This solution then is partially neutralized with sodium hydroxide to pH 3-4 in step 3 to precipitate Th-containing mud (thorium hydroxide). Then, the solution is treated with ammonium oxalate to convert the rare earth metal sulfates to their insoluble oxalates. Then, in step 4, the oxalates are converted to oxides by calcination. The oxides are dissolved in nitric acid represented by Solution (Ln⁺³) to obtain the rare earth metal (e.g. Ln). Only, cerium is insoluble in HNO₃ and separated at this stage.

[0034] Example 2:

Almost 65% of the rare earths used in the United States and Western Europe are consumed in catalysts mainly as FCC catalysts. The application of rare earths in FCC catalysts was motivated by the need for more active and hydrothermally stable products with better yield performance. Rare earth oxides (REO) completed these goals by enhancing catalytic activity and avoiding loss of acid sites during the standard procedure. Manufacturing costs of consumer goods that contain rare earth elements (REEs) may continue to decline per unit of output even as raw material costs continue to rise. Because the materials intensity (small amounts per unit output) of REEs is relatively low for most end-use applications (e.g. in FCC -1=3%), low-cost manufactured goods may contain high-cost materials (heavier REEs). Thus further processing, refining, and manufacturing capacity is necessary to meet growing demand and efficiencies of their uses.

[0035] The present invention provides such opportunity as shown in Figure 3B where step D embodies a separation method pursuant to an embodiment of the invention.

[0036] In step D, the “Monazite” oxalates from step 3 of the solvent extraction process of having rare earth metal amounts shown in the box (C) of Figure 3A are treated using the aqueous solution described above in which the HREEs oxalates (heavy rare earth oxalates) are soluble and the LREEs oxalates (light rare earth oxalates) are insoluble, thus separating the HREEs from the LREEs. The residue containing LREE (e.g. La, Nd, Pr, Sm oxalates) are calcined to convert them to oxides for use as FCC catalysts.

[0037] The present invention is advantageous in that chemical separation of

lanthanide oxalates within two groups: La-Sm (low-priced) and Gd-Lu (high-priced) is achievable in a 'one step' separation process, which takes a few minutes as compared to hours. Method embodiments of the invention are cost effective since the required materials (oxalic acid and the respective organic base) as well as the whole process are cheaper compared to the state-of-art solvent extraction with organophosphorus compounds. Moreover, method embodiments are simple and fast and need no special equipment or extreme synthetic conditions for the extractant preparation.

[0038] While the invention has been described in terms of specific embodiments thereof, it is not intended to be limited thereto but rather only to the extent set forth in the following claims.

CLAIMS

WE CLAIM

1. A method of separating rare earth metal oxalates, comprising mixing the rare earth metal oxalates and an aqueous solution comprising oxalic acid and an organic base wherein at least one rare earth metal oxalate is soluble and at least another rare earth metal oxalate is not soluble in the aqueous solution.
2. The method of claim 1 wherein the rare earth metal oxalates include at least one light rare earth metal oxalate and at least one heavy rare earth oxalate.
3. The method of claim 2 wherein the light rare earth oxalate includes at least one of La through Sm of the Periodic Table of Elements.
4. The method of claim 2 wherein the heavy rare earth oxalate includes at least one of Gd through Lu of the Periodic Table of Elements.
5. The method of claim 1 wherein the rare earth metal oxalates include different heavy rare earth metal oxalates.
6. The method of claim 5 wherein the different heavy rare earth metals include at least one of Gd, Tb, and Dy and at least one of Tm, Yb, and Lu.
7. The method of claim 1 wherein the oxalic acid comprises 5 to 95 mole % and the organic base comprises 95 to 5 mole % of the solution.
8. The method of claim 7 wherein the oxalic acid comprises 30 to 40 mole % and the organic base comprises 60 to 70 mole % of the solution.
9. The method of claim 8 wherein the oxalic acid comprises 32 to 34 mole % and the organic base comprises 66 to 68 mole % of the solution.
10. The method of claim 1 wherein the organic base is selected from the group consisting of N-containing organic base, or P-containing organic base, or S-containing organic base.
11. The method of claim 1 wherein the organic base comprises 1-methylimidazole.
12. In the solvent extraction method of rare earth metals wherein rare earth metal oxalates are formed, the step of separating the rare earth metal oxalates by mixing the rare earth metal oxalates and an aqueous solution comprising oxalic acid and an organic base so that at least one rare earth metal oxalate is soluble and at least another rare earth metal oxalate is not soluble.
13. The method of claim 12 wherein the rare earth metal oxalates include at least

- one light rare earth metal oxalate and at least one heavy rare earth oxalate.
14. The method of claim 12 wherein the light rare earth oxalate includes at least one of La through Sm of the Periodic Table of Elements.
 15. The method of claim 12 wherein the heavy rare earth oxalate includes at least one of Gd through Lu of the Periodic Table of Elements.
 16. The method of claim 12 wherein the rare earth metal oxalates include different heavy rare earth metal oxalates.
 17. The method of claim 16 wherein the different heavy rare earth metals include at least one of Gd, Tb, and Dy and at least one of Tm, Yb, and Lu.
 18. The method of claim 12 wherein the oxalic acid comprises 5 to 95 mole % and the organic base comprises 95 to 5 mole % of the solution.
 19. The method of claim 18 wherein the oxalic acid comprises 30 to 40 mole % and the organic base comprises 60 to 70 mole % of the solution.
 20. The method of claim 19 wherein the oxalic acid comprises 32 to 34 mole % and the organic base comprises 66 to 68 mole % of the solution.
 21. The method of claim 12 wherein the organic base is selected from the group consisting N-containing organic base, or P-containing organic base, or S-containing organic base.
 22. The method of claim 21 wherein the organic base comprises 1-methylimidazole.

1/2

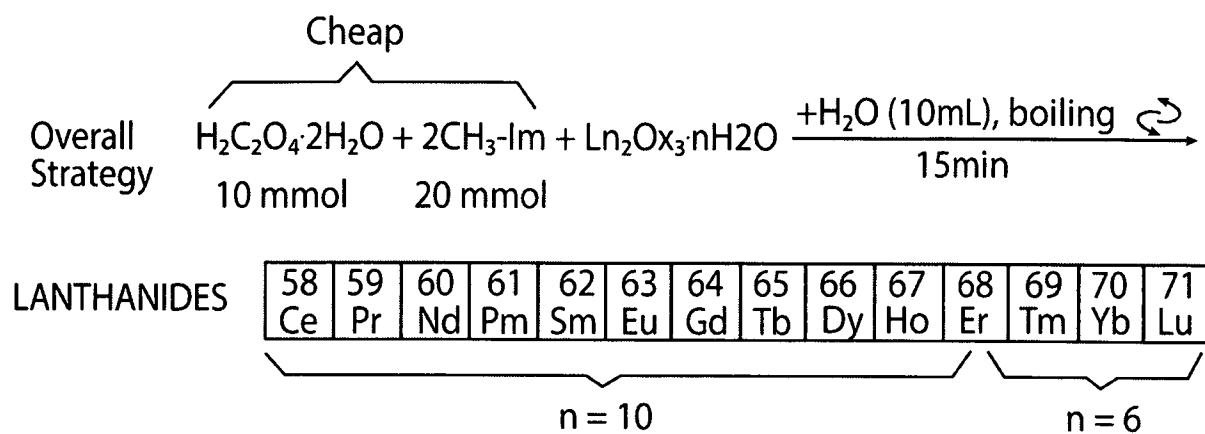


FIG. 1

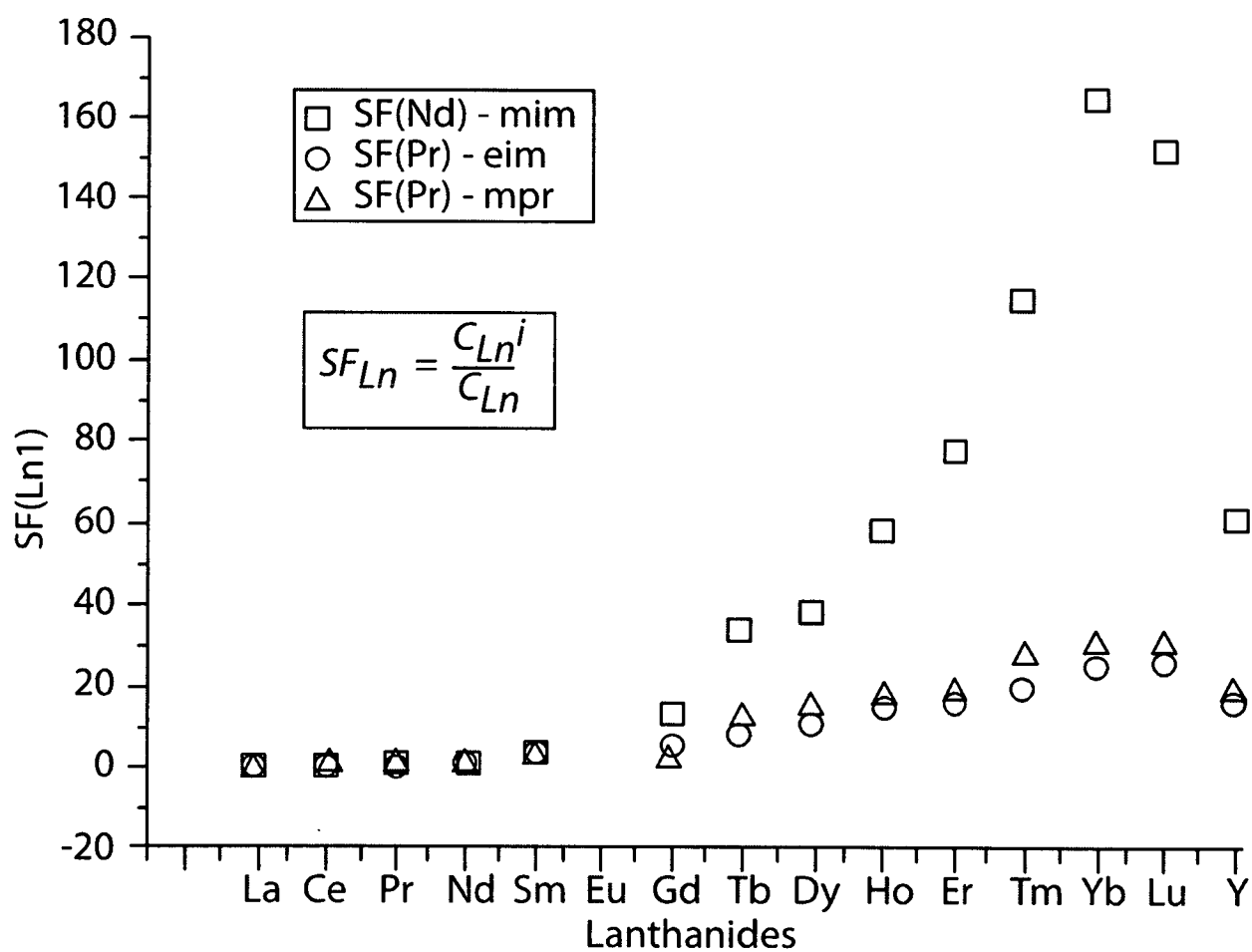
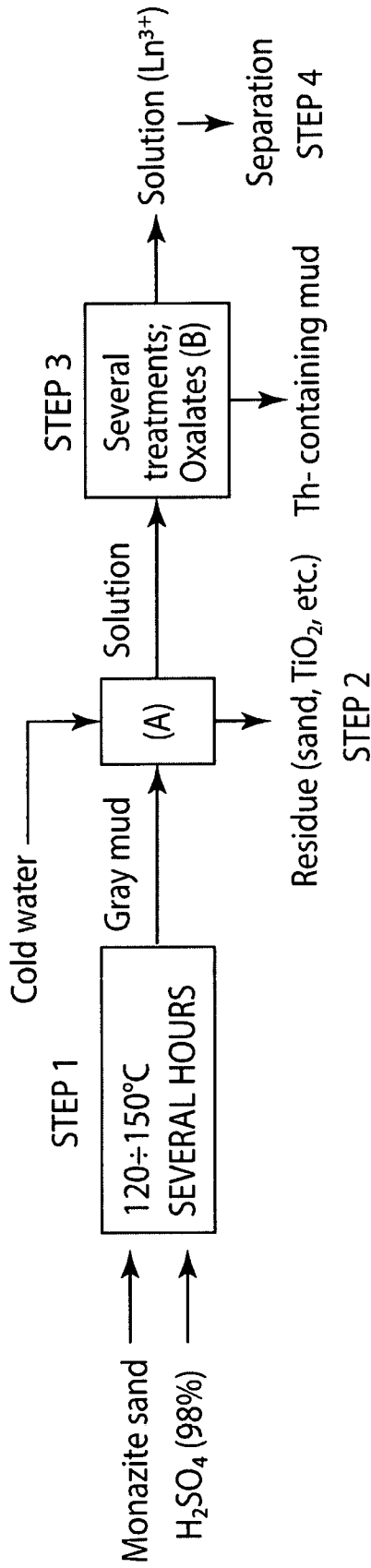


FIG. 2



A ≡ water-soluble sulfates of rare earths;

B ≡ the acidic filtrates are partially neutralized with sodium hydroxide to pH 3-4. Thorium precipitates out of solution as the hydroxide and is removed. After that, the solution is treated with ammonium oxalate to convert rare earths to their insoluble oxalates. The oxalates are converted to oxides by calcination. The oxides are dissolved in nitric acid. Only, cerium is insoluble in HNO_3 and separated here.

FIG. 3A

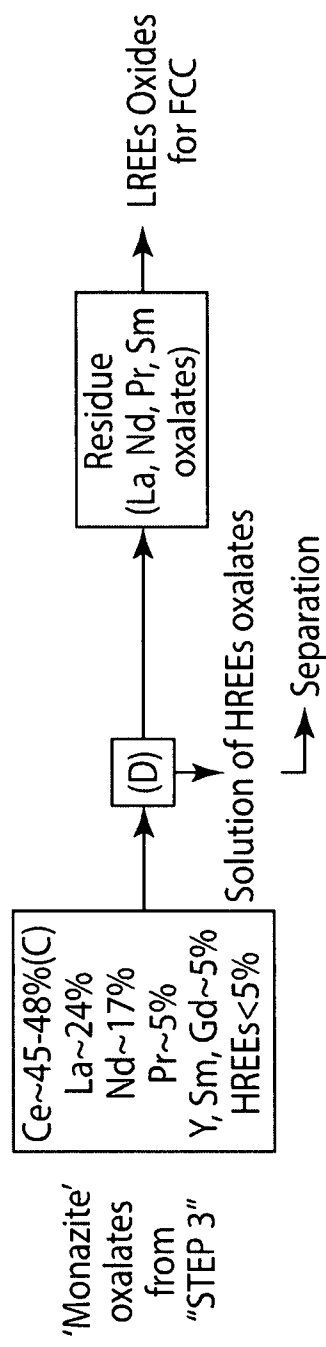


FIG. 3B

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2017/000040**A. CLASSIFICATION OF SUBJECT MATTER****C07F 5/00(2006.01)i, B01D 11/04(2006.01)i**

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

B. FIELDS SEARCHEDMinimum documentation searched (classification system followed by classification symbols)
C07F 5/00; C01F 17/00; C22B 3/46; C22B 59/00; C07C 55/07; B24B 1/00; B01D 11/04Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility modelsElectronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: rare earth metal oxalate, oxalic acid, organic base, heavy rare earth oxalate, light rare earth oxalate**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	AHMED, SHERIEN H. et al., 'Preliminary Study for Separation of Heavy Rare Earth Concentrates from Egyptian Crude Monazite', World Academy of Science, Engineering and Technology, 2014, Vol. 8, No. 8, pp. 866-872 See page 867, left column, paragraphs 3-6; abstract.	1-22
A	US 2015-0354026 A1 (RARE ELEMENT RESOURCES LTD.) 10 December 2015 See claim 1.	1-22
A	US 2009-0035202 A1 (HIRAIWA, TADASHI et al.) 05 February 2009 See paragraphs [0036]-[0037].	1-22
A	WO 03-104149 A1 (SHOWA DENKO K.K.) 18 December 2003 See claim 1.	1-22
A	KR 10-0174278 B1 (RHONE-POULENC CHIMIE) 18 February 1999 See claims 1-3.	1-22



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"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)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"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

"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

"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

"&" document member of the same patent family

Date of the actual completion of the international search

07 November 2017 (07.11.2017)

Date of mailing of the international search report

07 November 2017 (07.11.2017)

Name and mailing address of the ISA/KR

International Application Division

Korean Intellectual Property Office

189 Cheongsa-ro, Seo-gu, Daejeon, 35208, Republic of Korea

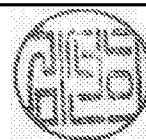


Facsimile No. +82-42-481-8578

Authorized officer

KIM, Sun Hee

Telephone No. +82-42-481-5405



INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2017/000040

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2015-0354026 A1	10/12/2015	AU 2014-207355 A1 CA 2898612 A1 EP 2946024 A2 EP 2946024 A4 RU 2015134576 A US 2014-0341790 A1 US 2016-0002751 A1 WO 2014-113742 A2 WO 2014-113742 A3 WO 2015-191645 A1	20/08/2015 24/07/2014 25/11/2015 30/11/2016 28/02/2017 20/11/2014 07/01/2016 24/07/2014 12/11/2015 17/12/2015
US 2009-0035202 A1	05/02/2009	CN 101155891 A CN 101155891 B JP 3929481 B2 TW 200704761 A US 7722692 B2 WO 2006-107116 A1	02/04/2008 04/07/2012 13/06/2007 01/02/2007 25/05/2010 12/10/2006
WO 03-104149 A1	18/12/2003	AU 2003-238154 A1 CN 100402431 C CN 101353178 A CN 101353178 B CN 101357776 A CN 1675131 A JP 2004-175652 A JP 4248937 B2 TW 200403188 A	22/12/2003 16/07/2008 28/01/2009 06/07/2011 04/02/2009 28/09/2005 24/06/2004 02/04/2009 01/03/2004
KR 10-0174278 B1	18/02/1999	CA 2041755 A1 CA 2041755 C CN 1056098 A EP 0455529 A1 EP 0455529 B1 FR 2661674 A1 US 5518703 A	05/11/1991 14/12/1999 13/11/1991 06/11/1991 22/03/1995 08/11/1991 21/05/1996