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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
3 June 2010 (03.06.2010)

PCT

(10) International Publication Number
WO 2010/062731 A1

(51) International Patent Classification:
B01D 59/18 (2006.01) *B01D 59/20* (2006.01)

(21) International Application Number:
PCT/US2009/063040

(22) International Filing Date:
3 November 2009 (03.11.2009)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/110,650 3 November 2008 (03.11.2008) US
12/603,748 22 October 2009 (22.10.2009) US

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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, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, 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, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (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, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

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

(54) **Title**: PRODUCTION OF NUCLEAR GRADE ENRICHED GADOLINIUM AND ERBIUM USING VOLATILE GD ER SPECIES USING AN AERODYNAMIC PROCESS

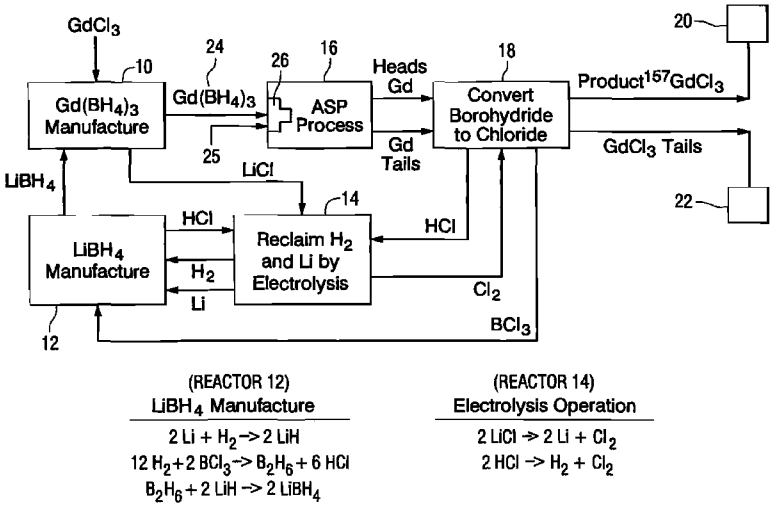


FIG. 1

(57) **Abstract**: A method of making Gd or Er isotopes from gaseous compounds containing $-BH_4$ and $-CH_3BH_3$ ions involves making the Gd or Er compounds (24) in a solid state reactor (10), passing the gaseous compounds (24) to a separation process (16) to provide products enriched in the desired isotopes of Gd or Er heads and Gd or Er tails depleted in these desired isotopes and then reacting the Gd or Er heads and Gd or Er tails with chlorine in a reactor (18) to provide products of $^{157}GdCl_3$, $^{155}GdCl_3$ or $^{167}ErCl_3$ enriched in Gd and Er isotopes.

WO 2010/062731 A1

PRODUCTION OF NUCLEAR GRADE ENRICHED GADOLINIUM AND ERBIUM USING VOLATILE GD OR ER SPECIES USING AN AERODYNAMIC PROCESS

Cross Reference To Related Application

This application claims priority under 35 U.S.C. §119 to U.S. Provisional Patent Application Serial No. 61/110,650, filed November 3, 2008 entitled, PRODUCTION OF NUCLEAR GRADE ENRICHED GADOLINIUM USING VOLATILE Gd SPECIES FROM AN AERODYNAMIC PROCESS.

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001] The invention relates to use of Gd and Er volatile molecules in the production of Gd and Er isotopes in an aerodynamic separation process.

2. Description of the Prior Art

[0002] Processes for separation of vapor phase isotope mixtures utilizing, in part, nozzle-like openings are well known in the art and taught, for example, in U.S. Patent No. 2,951,554 (*Becker*). Enhanced nozzle separation is taught in U.S. Patent Nos. 5,255,404 and 4,297,191 (both *Chen*). Double deflection nozzles are taught in U.S. Patent No. 4,551,157 (*Becker et al.*). The main problem in using these techniques for separating the isotopes of gadolinium and others below is the lack of a volatile molecule containing gadolinium.

[0003] In *Biro* (U.S. Patent No. 4,565,556), molecular and isotropic fractionating processes for gaseous mixtures are described. The gas mixture to be fractionated is subjected to a helicoidal path and interfered in its free circulation by means of aerodynamic elements to obtain fractions of different weights.

[0004] Isotope separation has been practically limited to a few elements due to the fact that the methods commonly available such as nozzle separation, centrifuge or diffusion require a stable, volatile feed material. The use of molecular laser isotope separation (MLIS), such as generally shown in U.S. Patent No. 3,951,768 (*Gürs*,) provides even more limitations. In addition to requiring a stable compound that is volatile, the compound must also possess absorption bands that are isotopically active in order to work. The use of atomic vapor laser

isotope separation (AVLIS) eliminates the need for stable volatile compounds but has difficulties in that the boiling point of gadolinium metal is ~3200°C which is difficult to achieve and that making a product that can be readily separated when activated due to its very fine particle size. In addition, AVLIS operations usually require at least two colors of operation (infra red IR) as well as ultra violet (UV)) wavelengths which tremendously increases costs as well as introducing technical issues with timing and product separation. Isotope separation using activation of a chemical reaction or delayed nucleation (CRISLA) are also known and generally taught in U.S. Patent No. 5,108,566 (*Eerkens*).

[0005] Isotope separation by ion cyclotron resonance (ICR) is also taught by *Louvet* in U.S. Patent No. 5,422,481. This method of separation, while technically feasible, is economically unattractive due to its very low production rate and very high capital investment. In addition, the very high boiling point of gadolium and erbium makes this approach very difficult. Producing isotopically separated gadolinium, uranium and many other elements has been a particular problem in this regard. There are many elements with no known, simple (and therefore economic to produce) volatile and stable compounds to work with. Those that have been identified have huge molecular weights such that the weight difference between the different isotopes is very small and the isotopic separation difficulty therefore increases.

[0006] Uranium isotope separation has been taught, for example, in U.S. Patent No. 4,097,384, where attractive volative uranium compounds for use in isotope separation include $U(By_4)_4$; $H_2C(C_5H_4)_2U(BY_4)_2$; $(C_5H_5)_3U(BY_4)$; $(CH_3H_5)_3U(BY_3C_2H_5)$ and $(C_4H_4N)_3U(BY_4)$ where Y=H or D (deuterium). Most lower molecular weight Gadolinium compounds (valance +3) are solids: $GdCl_3$, $6H_2O$ m.w. 371.76-wh.pr; GdF_3 m.w. 214.30 gelat; Gd_2O_2 m.w. 362.60 amor.powd.; and Gd_2S_2 m.w. 410.78 yel.mass.h.yg. Most lower weight Erbium compounds (valence +3) are solids: $Er(NO_3)_3$ $6H_2O$ m.w. 461.76 red. cr; and ER_2O_3 m.w. 383.28 red powd. (Concise Chemical and Technical Dictionary, Ed. H. Bennett, 1962, pp. 368 and 420-421).

[0007] Gadolinium and also erbium are extremely valuable rare earth metal isotopes, for use as neutron ("poison") absorbers in nuclear reactors, as is well known in the art, and are important to the nuclear industry. Gd^{157} has excellent neutron absorption capabilities, as described in U.S. Patent No. 7,318,899 (*Lemaire et al.*) where such isotopes are separated in an aqueous medium by treating soluble compounds of gadolinium with a ligand designed to

complex with at least one of the isotopes and nanofiltering the treated aqueous medium to separate the isotopes. A somewhat similar process was described in U.S. Patent No. 5,470,479 (*Snyder et al.*). U.S. Patent 5,595,714 (*Ripa et al.*) also involves recovery of Gd and its complexing agents from aqueous solutions. *Paisner et al.* (U.S. Patent No. 5,202,005) also recognized the importance of Gd^{157} and Gd^{155} as useful burnable poisons in light water nuclear power reactors. They were enriched by selective photoionization using linear parallel polarized laser beam energy.

[0008] Gd and Er "burnable absorbers" which absorb neutrons during nuclear fission, whose ability to absorb neutrons decreases with increased exposure to nuclear fission are recognized by *Grossman et al.* (U.S. Patent No. 5,350,542) are separated by atomic vapor laser isotope separation (AVLIS) developed at the Lawrence Livermore National Laboratory. Problems with AVLIS were generally discussed earlier.

[0009] *Peterson, Lahoda and Weisberg*, in U.S. Patent No. 4,711,768 taught use of a liquid chromatographic column system using an ion-exchange resin and eluent solution to separate Gd isotopes, which Gd is used for nuclear control rods and burnable poison shims, preferably Gd^{155} and Gd^{157}. Problems herein include the low degree of separation per stage (leading to very large and uneconomic columns due to the high cost of the ion-exchange resin) and the low production rate due to the batch operation of the separation column.

[0010] Finally, *Snyder et al.* (U.S. Patent No. 5,470,479) teaches continuous separation of isotopes of Gd. This method is again not economically feasible because of the very small separation factors that were achieved per theoretical stage.

[0011] None of these patents address using gaseous $Gd(BH_4)_3$ or similar gaseous Er compounds, in an injector nozzle separation device, to produce isotopes of Gd or Er. Again, the reason for this has been the lack of a volatile low molecular weight compound containing gadolinium or erbium.

[0012] It is a main object of this invention to provide a method of using gaseous Gd or Er compounds in a process to provide useful Gd and Er isotopes.

SUMMARY OF THE INVENTION

The above needs have been met and problems solved by providing a method where highly volatile compounds of gadolinium and erbium containing three-BH_4 or -CH_3BH_3, ligands/ions, hereinafter "(Gd, Er)·(-BH_4, -CH_3BH_3)$_3$ compounds" preferably Gd or Er with -BH_4, are used in an aerodynamic separation process to separate isotopes of gadolinium or erbium. The term aerodynamic separation process ("ASP") is herein defined to mean any gas flow separation device such as that described in *Biro* (U.S. Patent No. 4,565,556), in U.S. Patent No. 2,951,554 (*Becker*), in U.S. Patent No. 5,255,404 (*Chen*), U.S. Patent No. 4,297,191 (*Chen*) or double deflection nozzles as taught in U.S. Patent No. 4,551,157 (*Becker et al.*). A carrier gas is used in the ASP process, and is selected from the group consisting of H_2, He and mixtures thereof, preferably at a temperature range of between -50°C and 400°C, at pressures from vacuums such as 0.001 atmospheres, to pressures up to 100 atmospheres.

[0013] In the method, (Gd, Er)·(-BH_4, -CH_3BH_3)$_x$, where $_x$ = 3 is manufactured as a gaseous starting product or starting "Product". That starting Product is passed to an ASP process, as generally described previously to provide Gd or Er heads and Gd or Er tails. The term "heads" means a product enriched in the concentration of the desired isotopes. The term "tails" means a waste stream depleted in the concentration of the desired isotopes. These heads and tails are then reacted with Cl_2 gases. This is generally shown in the FIGS.

[0014] More specifically, the invention preferably utilizes $Gd(BH_4)_3$ or $Er(BH_4)_3$ and involves a method of providing gaseous Gd or Er isotopes comprising: (a) reacting a solid starting product material selected from the group consisting of $GdCl_3$ or $ErCl_3$ in a reactor with $LiBH_4$ to provide a reaction product selected from the group consisting of gaseous $Gd(BH_4)_3$, or gaseous $Er(BH_4)_3$ and solid LiCl; (b) passing the gaseous reaction product into an aerodynamic separation process utilizing an injector nozzle in a stationary reactor to produce centrifugal force/spiraling or swirling gases while utilizing a carrier gas selected from the group selected from the group consisting of H_2, He and mixtures thereof, to provide heads and tails selected from the group selected from Gd or Er heads and Gd or Er tails; and (c) passing the heads and tails to a reactor to react with Cl_2 to provide BCl_3 and HCl off gases and final solid product selected from the group consisting of $^{157}GdCl_3$, $^{155}GdCl_3$ and $^{167}ErCl_3$ rich in Gd and Er isotopes.

[0015] In the above method, the BCl_3 and HCl off gases from step (c) are passed to an electrolysis unit where LiCl from step (a) is reacted with HCl from a separate reactor where H_2 and Li from the electrolysis unit and BCl_3 from step (c) are reacted to provide $LiBH_4$ which is fed into step (a) and HCl which is passed to the electrolysis unit.

BRIEF DESCRIPTION OF THE DRAWINGS

[0016] A further understanding of the invention can be gained from the following description of the preferred embodiments when read in conjunction with accompanying drawings in which:

[0017] FIG. 1 is a simple, block diagram of the method of this invention involving Gd (valence = +3) isotope separation using a $-BH_4$ ligand; and

[0018] FIG. 2 is a simple, block diagram of the method of this invention involving Er (valence = +3) isotope separation using a $-BH_4$ ligand.

DESCRIPTION OF THE PREFERRED EMBODIMENT

[0019] Gd and Er compounds are synthesized using $-BH_4$ or $-(CH_3BH_3)$ ligands/ions. These compounds of gadolinium and erbium have overcome all the barriers described in the BACKGROUND above. These compounds are relatively stable, have low molecular weights and are simple to produce. Boron (B) has two isotopes with concentrations of 19.9% of B10 and 80.1% of B11. In order to improve the per pass yield in the separation step, a single isotope of boron or more likely an isotopic mix that is enriched in either B10 or B11, could be used (see for instance, 5,443,732 "Boron isotope separation using continuous ion exchange chromatography" or 5,419,887 "Separation of the isotopes of boron by chemical exchange reactions".) The term "isotropic mix" means the same element with more than one isotope.

[0020] In addition, the use of an aerodynamic separation process to produce a Gd product enriched in Gd157 isotopes overcomes the issues associated with other isotope separation processes. For erbium, the Er167 isotope would be enriched. The aerodynamic process utilizes compressors to increase carrier gas pressure that contains the volatile form of Gd or other element, and carrier gas 25 (either He or H_2, or their mixture) is then injected by injector nozzle separation device 26 at pressures between 0.001 atmospheres to 100 atmospheres,

preferably 2 atmospheres to 10 atmospheres to affect a spinning/swirling motion in the gas, that results in the centrifugal separation of the isotope of Gd or other element of interest by centrifugal force. The carrier gas temperature can range from -50°C to 400°C, preferably from 25°C to 200°C. The process does not break bonds, forming lower molecular weight volatile species that are hard to collect and separate from the products as do laser isotope separation methods. It has a much lower cost than diffusion methods. The process can also operate at elevated temperatures, where actual centrifuges are not operable. The process of this invention involves a gas swirling around inside a tank rather than spinning the tank, as well as lower temperatures, for instance -50°C. So, for example, it is possible to operate at any elevated temperature such as up to 400°C, which allows sufficient volatility of the compound whose isotope is being separated. The pressures that are used in the process would range from vacuums of about 0.001 atmospheres to pressures up to 100 atmospheres, as previously mentioned.

[0021] In this invention, referring to FIG. 1, treating the preferred material Gd, $GdCl_3$ is reacted with $LiBH_4$ by ball-milling them together at atmospheric pressure at room to slightly elevated (100°C) in a water vapor free enclosure to provide $Gd(BH_4)_3$ ("Product": 24) in a reactor 10. The $LiBH_4$ is manufactured in reactor 12 by combining BCl_3, Li and H_2 according to the reactions:

$2Li + H_2 \rightarrow 2LiH$; $12H_2 + 2BCl_3 \rightarrow B_2H_6 + 6HCl$, and

$B_2H_6 + 2LiH \rightarrow 2LiBH_4$.

[0022] The Li is produced in reactor 14, in an electrolysis process, wherein LiCl product from reactor 10 and HCl product from reactor 12 are reacted with HCl, with the overall reactions:

$2LiCl \rightarrow 2Li + Cl_2$, and

$2HCl \rightarrow H_2 + Cl_2$.

[0023] In the ASP process reactor 16, preferably the $Gd(BH_4)_3$ or $Er(BH_4)_3$, or other "Product," is mixed with carrier gas (hydrogen and/or helium) and raised to pressures of preferably 2 to 10 atmospheres at temperatures from 25°C to 400°C. The carrier gas with product is then injected through nozzles 26 and into a stationary, non-spinning collection chamber, generating sufficient centrifugal forces to cause gas swirling and separation of the various isotopes of the gadolinium or erbium.

[0024] Subsequently, Gd heads and Gd tails, previously defined, are fed to a separate reactor 18 to convert borohydride to chloride by reaction with Cl_2 feed, to form BCl_3 and $^{157}GdCl_3$ or $^{155}GdCl_3$ heads (product 20) and $GdCl_3$ tails (product 22). $GdCl_3$ is a solid and will therefore separate readily from the Cl_2, HCl and BCl_3. These reactions will be viable with all components of (Gd, Er)·(-BH_4, -CH_3BH_3)$_3$ components.

[0025] An electrolysis process 14 is used in this invention to convert the LiC to Cl_2 which is fed to reactor 18, and H_2 and Li is fed to reactor 12.

[0026] FIG. 2 provides a similar process for utilizing Er (valence +3, the same as Gd). Such reactions are completely similar; only Er is substituted for Gd in the process. This FIG. 2 is incorporated into the specification as a duplicate of FIG. 1 with all reaction parameters in reactors 30, 32, 36 and 38 being the same and providing similar products 40; $^{167}ErCl_3$ and tails 42. Er $(BH_4)_3$ starting Product is shown as 44, the injector as 46 and the electrolysis reactor as 34.

[0027] Thus, Gd157, Gd155, and Er167 are isotopes of Gd or Er and the product heads are rich in those isotopes in the chemical form of $GdCl_3$ or $ErCl_3$ and the waste tails are depleted in those isotopes in the chemical form $GdCl_3$ or $ErCl_3$.

[0028] While specific embodiments of the invention have been described in detail, it will be appreciated by those skilled in the art that various modifications and alternatives to those details could be developed in light of the overall teachings of the disclosure. Accordingly, the particular embodiments disclosed are meant to be illustrative only and not limiting as to the scope of the invention which is to be given the breath of the appended claims and any and all equivalents thereof.

What is claimed is:

1. A method for separation of the isotopes of Gd and Er from gaseous Gd and Er compounds containing $-BH_4$ or $-CH_3BH_3$ ligands in an aerodynamic separation process comprising the steps of:

(a) making the Gd or Er compounds with high volatility that are put into a gaseous state;

(b) passing the gaseous Gd or Er compounds to an aerodynamic separation process to provide Gd or Er heads and Gd or Er tails; and then

(c) reacting the Gd or Er heads and Gd or Er tails with chlorine to produce either solid $GdCl_3$ or $ErCl_3$ product enriched in Gd or Er isotopes.

2. The method of Claim 1, wherein isotopically separated boron (B) is used to maximize the yield of the aerodynamic separation process.

3. The method of Claim 1, wherein a carrier gas selected from the group consisting of H_2, He and mixtures thereof is used in the aerodynamic separation process of step (b).

4. The method of Claim 3, wherein the carrier gas is at temperatures between -50°C and 400°C in the aerodynamic separation process.

5. The method of Claim 3, wherein the carrier gas is at pressures between 0.001 atmospheres and 100 atmospheres in the aerodynamic separation process.

6. The method of Claim 1, wherein Gd compounds are made in step (a) and the product in step (c) is a mixture of $GdCl_3$ enriched in the isotopes of ^{157}Gd and/or ^{155}Gd.

7. The method of Claim 1, wherein Er compounds are made in step (a) and the product in step (c) is a mixture of $ErCl_3$ enriched in the isotopes of ^{167}Er.

8. The method of Claim 1, wherein the ligand is $-BH_4$.

9. A method of providing solid gaseous $GdCl_3$ and $ErCl_3$ enriched in the desired isotopes comprising:

(a) reacting a solid starting product material selected from the group consisting of $GdCl_3$ or $ErCl_3$ in a reactor with $LiBH_4$ to provide a reaction product selected from the group consisting of gaseous $Gd(BH_4)_3$ or gaseous $Er(BH_4)_3$ and solid LiCl;

(b) passing the gaseous reaction product with a carrier gas selected from the group consisting of H_2, He and mixtures thereof into an aerodynamic separation process utilizing an injector nozzle in a stationary reactor to produce centrifugal force to provide a heads product and tails product where the heads product is enriched in one or more of the isotopes ^{155}Gd, ^{157}Gd or ^{167}Er; and

(c) passing the heads and tails to a reactor to react with Cl_2 to provide BCl_3 and HCl off gases, and final solid product containing one or more enriched products, containing enriched isotopes, the products selected from the group consisting of $^{157}GdCl_3$ $^{155}GdCl_3$ and $^{167}ErCl_3$.

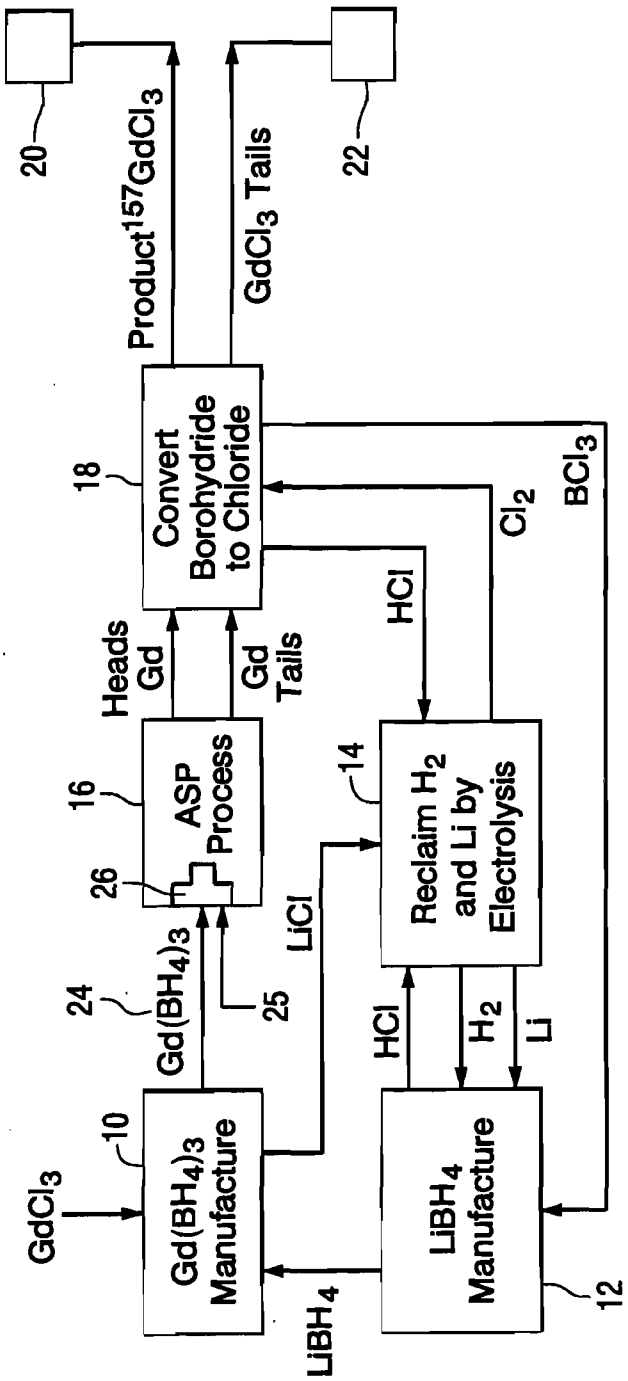
10. The method of Claim 9, wherein the BCl_3 and HCl off gases from step (c) and LiCl from step (a) are passed to an electrolysis unit where H_2, Cl_2 and Li are formed.

11. The method of Claim 10, wherein Li and H_2 from the electrolysis unit and BCl_3 from step (c) are used to make $LiBH_4$ which is fed into step (a), and HCl which is passed to the electrolysis unit.

12. The method of Claim 9, wherein the carrier gas in step (b) is at a temperature between -50°C and 400°C.

13. The method of Claim 9, wherein the carrier gas is at a pressure between 0.001 atmospheres and 100 atmospheres.

14. The method of Claim 9, wherein the aerodynamic process causes gas swirling.



(REACTOR 12)
$LiBH_4$ Manufacture

$2\,Li + H_2 \rightarrow 2\,LiH$

$12\,H_2 + 2\,BCl_3 \rightarrow B_2H_6 + 6\,HCl$

$B_2H_6 + 2\,LiH \rightarrow 2\,LiBH_4$

(REACTOR 14)
Electrolysis Operation

$2\,LiCl \rightarrow 2\,Li + Cl_2$

$2\,HCl \rightarrow H_2 + Cl_2$

FIG. 1

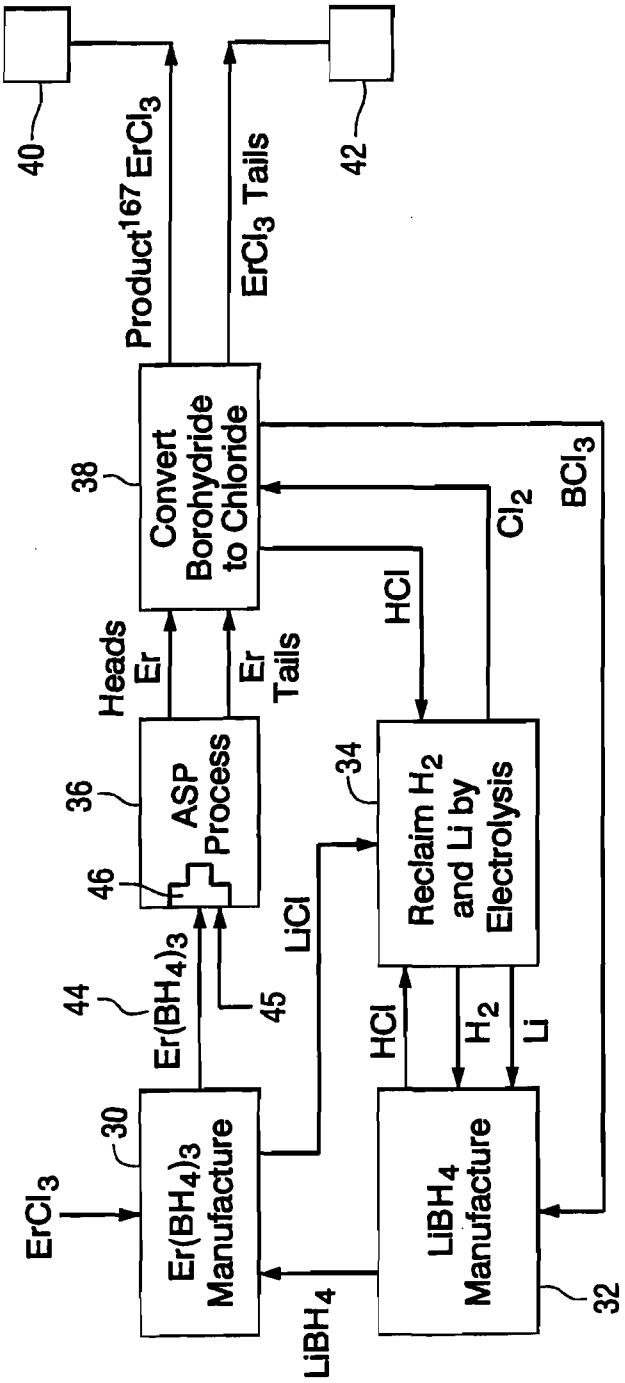

40
Product 167 $ErCl_3$
$ErCl_3$ Tails
42
38
Convert Borohydride to Chloride
Heads Er
Er Tails
HCl
Cl_2
BCl_3
36
ASP Process
46
34
Reclaim H_2 and Li by Electrolysis
44
$Er(BH_4)_3$
45
LiCl
HCl
H_2
Li
$ErCl_3$
30
$Er(BH_4)_3$ Manufacture
$LiBH_4$
$LiBH_4$ Manufacture
32
(REACTOR 32)
$LiBH_4$ Manufacture
$2 Li + H_2 \rightarrow 2 LiH$
$12 H_2 + 2 BCl_3 \rightarrow B_2H_6 + 6 HCl$
$B_2H_6 + 2 LiH \rightarrow 2 LiBH_4$
(REACTOR 34)
Electrolysis Operation
$2 LiCl \rightarrow 2 Li + Cl_2$
$2 HCl \rightarrow H_2 + Cl_2$

FIG. 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2009/063040

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01D59/18 B01D59/20
ADD.

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)
B01D

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 437 795 A (SNYDER THOMAS S [US] ET AL) 1 August 1995 (1995-08-01) the whole document	1,9
A	US 5 470 479 A (SNYDER THOMAS S [US] ET AL) 28 November 1995 (1995-11-28) the whole document	1,9

☐ 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

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Date of the actual completion of the international search	Date of mailing of the international search report
5 March 2010	15/03/2010

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Brothier, J

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2009/063040

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