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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
16 January 2014 (16.01.2014)

WIPO | PCT

(10) International Publication Number
WO 2014/011455 A1

(51) International Patent Classification:
C01B 3/02 (2006.01) *B01J 19/24* (2006.01)
C01F 7/02 (2006.01)

(21) International Application Number:
PCT/US2013/049146

(22) International Filing Date:
2 July 2013 (02.07.2013)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/669,378 9 July 2012 (09.07.2012) US

(71) Applicant: **KAONETICS TECHNOLOGIES, INC.** [US/US]; P.O. Box 470398, Forth Worth, TX 76147 (US).

(72) Inventor: **ELTON, John A.**; 3319 E. Rosedale Lane, Unit D, Orange, CA 92869 (US).

(74) Agent: **VOSEN, Steven R.**; 1563 Solano Ave., #206, Berkeley, CA 94707 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

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

(54) Title: METHOD AND APPARATUS FOR PRODUCING HYDROGEN AND ALUMINUM OXIDE FROM ALUMINUM

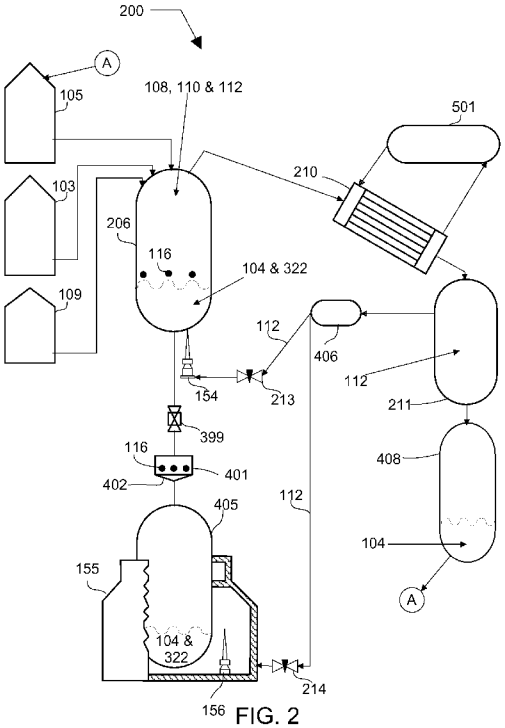


FIG. 2

(57) Abstract: A method and apparatus is provided for producing hydrogen and aluminum oxide, which may include alpha phase aluminum oxide, from aluminum and an acid. The aluminum may include contaminants, and the acid may be reclaimed and reused within the method or apparatus to reduce the use of resources. In addition, the hydrogen may be used to generate heat to drive the various chemical and physical processes used to produce aluminum oxide.

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METHOD AND APPARATUS FOR PRODUCING HYDROGEN AND ALUMINUM OXIDE FROM ALUMINUM

TECHNICAL FIELD

[0001] This application relates generally to aluminum recycling and hydrogen generation, and more specifically to a process and an apparatus for the generation of hydrogen and aluminum oxide from aluminum containing mixtures and acids while only requiring additional inputs of aluminum containing feedstock once the process is started.

BACKGROUND ART

[0002] Hydrogen can be generated by a variety of methods. However, generating hydrogen cheaply with little or no greenhouse gas (GHG) generation is the challenge facing today's hydrogen generation technology innovations. Hydrogen can be generated by natural gas reforming, coal gasification, electrolysis, thermal water splitting, biomass conversion and photo electrochemical methodologies. Natural gas reforming and coal gasification are mature technologies that are used by many industries, but these technologies generate greenhouse gases and in the future will require carbon sequestration. Electrolytic generation of hydrogen is also a mature technology, but it indirectly contributes to GHG generation unless renewable sources of energy such as wind and solar are utilized. Most of the other processes for hydrogen generation are not yet fully mature and require additional research and development to make them cost effective and/or technologically sound.

[0003] High purity alpha aluminum oxide is prized for its hardness, for its high melting temperature and especially for its use as the primary source in the production of aluminum. Bauxite is the main source of the feedstock material for the production of aluminum oxide by the Bayer process whereby hydrated aluminum oxide mixtures are converted to aluminum oxide. Corundum is produced by taking bauxite along with additional carbon and iron to above the melting point of the bauxite. The carbon and iron help remove impurities through chemical and separative processes and provide the hard alpha phase form of alumina, corundum. Both of these processes are quite mature having been used for many years. An alternative method to produce aluminum oxide is by reacting the bauxite ore with hydrochloric acid to produce aluminum chloride hexahydrate followed by heating the aluminum chloride hexahydrate to temperatures as high as 1500 °C.

[0004] Similarly, chlorinated and hydrated aluminum hydroxides of varying concentrations (basic aluminum chlorides) can be generated by the reaction of aluminum with hydrochloric acid. These reactions are exothermic with the evolution of heat and hydrogen.

[0005] Scrap aluminum is recycled typically by filtering the aluminum chemically and mechanically from other metals and non-metallic components and heating the aluminum remaining to temperatures exceeding the melting point of aluminum. This secondary aluminum is much less expensive than the aluminum obtained from the production of aluminum by the Hall-Heroult process. However, scrap aluminum with high percentages of metallic impurities or high percentages of non-metallic materials are typically difficult to recycle economically. There therefore exists a need for a process to recycle such low value scrap aluminum that is relatively economical and environmentally friendly.

[0006] Thus there is a need in the art for a method and apparatus that permits for the recycling of scrap aluminum and the generation of hydrogen. Such a method and apparatus should be easy and robust to use, be flexible enough to produce a range of products, be cost effective, and be able to accept a range of contaminants in input scrap aluminum.

DISCLOSURE OF INVENTION

[0007] The present invention overcomes the disadvantages of the prior art by providing a reactive means to generate hydrogen, regenerate the reactants other than aluminum and produce a byproduct that has value – aluminum oxide. Furthermore, the processes and devices of the present invention can perform these functions without the need for external energy sources, with the generation of additional work from the steam produced and with only scrap aluminum as feedstock once the process has been initiated.

[0008] Certain embodiments described herein react contaminated scrap aluminum with acid to produce hydrogen and a solution that can be processed to provide aluminum oxide. One embodiment regenerates the acid from the chlorinated aluminum oxide solution through a drying and heating methodology and calcines the resulting solid mixture to sufficient temperature to produce a calcined aluminum oxide. Several purification steps may be performed to remove significant amounts of impurities from solutions, aluminum chloride hexahydrate and calcined aluminum oxide to give a significantly purified and calcined aluminum oxide.

[0009] Various embodiments have certain advantages over the prior art. These include, but are not limited to:

- using aluminum containing mixtures as starting material – especially scrap aluminum – for the reaction with acid;
- regenerating acid by using internally generated heat due to the exothermic reaction and the burning of generated hydrogen; and
- generating a higher purity aluminum oxide such as corundum from the initial contaminated scrap aluminum. This higher purity is achieved by both reactive and separation processes and is best affected by using the heat generated in the reaction and a portion of the hydrogen generated for heating.

[0010] This process and device can be cycled with only additions of contaminated scrap aluminum once the process is initiated.

[0011] One embodiment provides a method for producing hydrogen and aluminum oxides from aluminum and contaminants. The method includes accepting a feedstock including contaminants other than aluminum; reacting the accepted feedstock with an acid to produce hydrogen and other products of reaction; forming aluminum oxide from the other products of reaction; and collecting the aluminum oxide. The method also includes performing one or more of collecting the hydrogen, and generating heat from the chemical energy in the hydrogen. The generated heat is provided to assist in one or more of: the reacting the accepted feedstock with acid and the forming aluminum oxide.

[0012] Another embodiment provides a method for producing hydrogen and aluminum oxides from aluminum with a regenerated acid. The method includes: accepting a feedstock including aluminum and/or aluminum oxide; reacting the accepted feedstock with an acid to produce hydrogen and other products of reaction; forming aluminum oxide from the other products of reaction; and collecting the aluminum oxide. The method further includes performing one or more of collecting the hydrogen, and generating heat from the chemical energy in the hydrogen. The generated heat is provided to assist in one or more of: the reacting the accepted feedstock with acid and the forming of aluminum oxide. The method further includes recovering regenerated acid from one or more of the reacting of the accepted

feedstock and the forming of aluminum; and providing the regenerated acid as the acid for the reacting of the feedstock and acid.

[0013] Yet another embodiment provides a device for producing hydrogen and aluminum oxides from a feedstock including aluminum and an acid. The device includes: a reaction vessel adapted to accept the feedstock and the acid and produce first gaseous products including hydrogen and non-gaseous products; a first heater for heating the reaction vessel; furnace collection vessel to accept the non-gaseous products and produce aluminum oxide and second gaseous products; a second heater for heating the furnace collection vessel; and a gas collection device to accept one or more of the first gaseous products and the second gaseous products; and an acid regeneration system to recover acid from the gas collection device and provide the regenerated acid to the reaction vessel. The device operates such that hydrogen and aluminum oxide may be produced using a regenerated acid.

[0014] These features together with the various ancillary provisions and features which will become apparent to those skilled in the art from the following detailed description, are attained by the system and method of the present apparatus and process, preferred embodiments thereof being shown with reference to the accompanying drawings, by way of example only, wherein:

BRIEF DESCRIPTION OF DRAWINGS

[0015] FIG. 1A is a schematic of an embodiment of a method for the generation of hydrogen and aluminum oxide from aluminum;

[0016] FIG. 1B is a schematic diagram showing a first embodiment of an apparatus for the generation of hydrogen and aluminum oxide from aluminum;

[0017] FIG. 1C is a schematic diagram showing a second embodiment of an apparatus for the generation of hydrogen and aluminum oxide from aluminum that is optimized for the generation of primarily alpha phase aluminum oxide by using all or a portion of the hydrogen generated by the process for heating purposes;

[0018] FIG. 1D is a schematic diagram showing a third embodiment of an apparatus for the generation of hydrogen and aluminum oxide from aluminum that is optimized for the generation of hydrogen and aluminum oxide with minimal external energy and power requirements;

[0019] FIG. 2 is a more detailed schematic of one embodiment of an apparatus that is generally similar to the embodiment of FIG. 1C;

[0020] FIG. 3 shows the embodiment of FIG. 2 as used for the regeneration of acid as the purified solution is heated to dryness;

[0021] FIG. 4 shows the embodiment of FIG. 2 as used for heating aluminum oxide to produce alpha phase aluminum oxide;

[0022] FIG. 5 illustrates the purification of the aluminum oxide of any magnetic components;

[0023] FIGS. 6 and 7 are more detailed schematics of another embodiment of an apparatus that is generally similar to the embodiment of FIG. 1B.

[0024] Reference symbols are used in the Figures to indicate certain components, aspects or features shown therein, with reference symbols common to more than one Figure indicating like components, aspects or features shown therein.

MODE(S) FOR CARRYING OUT THE INVENTION

[0025] Embodiments of the present invention are directed to the use of aluminum mixture, including scrap aluminum, to produce hydrogen and a final product such as aluminum oxide. Various embodiments described herein exemplify a range of embodiments ranging from a minimal process to extended processes that use more or less energy and/or produce other products.

[0026] Figure 1A is a schematic of an embodiment of a method **10** for the generation of hydrogen and aluminum oxide from aluminum. Method **10** is also referred to herein as the "MicroHyGen" or "MHG" process, for processing an aluminum-containing feedstock. The feedstock may, for example and without limitation, be aluminum and/or aluminum oxide, or may include a "scrap" aluminum that comprises contaminants other than aluminum. Contaminants which may be processed by method **10** include, but are not limited to, other metals, compounds including other metals, paper, or organic compounds.

[0027] Method **10** includes the steps of adding a feedstock (Block **11**), replenishing acid (Block **12**), replenishing water (Block **14**), and reacting the added or replenished feedstock and acid (Block **15**). Method **10** may also, when necessary, include adding heat (Block **13**),

which is also used in Block **15**. Method **10** also includes separating and collecting solid waste products (Block **16**), separating and collecting aluminum products (Block **17**), and separating and collecting hydrogen (Block **18**). In general, the flow of material is one-way, as indicated by the arrows between blocks, with the exception of the two-way flow of acid between Blocks **12** and **15**. In one alternative embodiment, hydrogen from Block **18** is provided to Block **13**, where the hydrogen is reacted to release heat, as indicted by the dashed line between Blocks **13** and **18**. In another alternative embodiment, steam that is generated in Block **15** and or Block **13** is provided to Block **19**, where the steam is used to generate energy, such as electric power.

[0028] In a steady state operation, the feedstock and heat are provided for the reactions in Block 15 (Blocks **11** and **13**, respectively) and valuable aluminum products and hydrogen are generated and collected (Blocks **17** and **18**, respectively). Block **12** allows for control of the acid concentration or level in Block **15** by accepting or providing acid, as indicated by the arrows. Block **14** allows for replenishing water in Block **15**.

[0029] In one embodiment, the feedstock in Block **11** contains contaminants, which are recovered as waste in Block **16**, the acid replenished in Block **12** is hydrochloric acid, the aluminum separated and collected in Block **17** is aluminum oxide.

[0030] In certain embodiments, the reactions within Block **15** may include a first reaction, as in Block **15a**, wherein the feedstock from Block **11** reacts with an aqueous hydrochloric acid solution from Block **12** and heat from Block **13** to generate hydrogen and a chlorinated aluminum oxide solution, and a second reaction, as in Block **15b**, where the chlorinated aluminum oxide solution from Block **15a** is heated with heat from Block **13** to create a mixture of waste and aluminum products, which are separated and collected in Blocks **16** and **17**, respectively.

[0031] Apparatus for the generation of hydrogen and aluminum oxide from an aluminum-containing feedstock using method **10** are illustrated in the schematic diagrams of FIGS. 1B, 1C, and 1D, where FIG. 1B shows a first embodiment as apparatus **100A**, Fig. 1C shows a second embodiment as apparatus **100B** optimized for the generation of primarily alpha phase aluminum oxide by using all or a portion of the hydrogen generated by the process for heating purposes, and FIG. 1D shows a third embodiment as apparatus **100C** optimized for

the generation of hydrogen and aluminum oxide with minimal external energy and power requirements.

[0032] Apparatus **100A**, **100B**, and **100C** each include a vessel **103** for storing an aluminum-containing feedstock, a vessel **105** for storing acid, a vessel **109** for storing water, a container **107** for collecting aluminum oxide, one or more heaters **111**, and a vessel **212** for collecting hydrogen. Reactions take place in one or more vessels **150**. As discussed subsequently, vessels **150** may be vessels in which the various reactants or byproducts of reaction are sequentially combined and reacted. FIGS. 1B, 1C, and 1D are labeled to show the relationship to method **10**, as including arrows indicating Blocks **11**, **12**, **13**, **14**, **15**, **16**, **17** and **18**.

[0033] Apparatus **100A** is an embodiment of a general method **10**. In one embodiment of apparatus **100A**, an aluminum-containing feedstock that includes contaminants other than aluminum reacts with hydrochloric acid and water to generate hydrogen and a chlorinated aluminum oxide solution in a first reaction vessel. The chlorinated aluminum oxide solution is then heated causing the acid to be regenerated and the formation of aluminum oxide in a second reaction vessel.

[0034] Apparatus **100B** is similar to apparatus **100A,** and provides hydrogen from vessel **212** to heater **111**. In certain embodiments, some or all of the generated hydrogen is used for heating to drive chemical reactions in vessels **150**. Apparatus **100B** is optimized for the generation of primarily alpha phase aluminum oxide because the hydrogen generated during reaction of the aluminum and acid is subsequently all or partially used for heating purposes.

[0035] Apparatus **100C** is similar to apparatus **100B,** and provides steam from vessels **150** and heater **111** to generator **113** for producing electricity from the steam which may, in turn, be used to power one or more various devices, such as motors, valves, and the like, of apparatus **100C**.

[0036] More detailed schematics of apparatus for performing some or all of the processes of method **10** and/or apparatus **100A**, **100B**, and **100C** are illustrated in Figures 2, 3, 4, 5, 6, and 7.

[0037] Figure 2 is a more detailed schematic of one embodiment of an apparatus **200** that is generally similar to apparatus **100B**, except as explicitly stated.

[0038] Apparatus **200** includes vessel **103** for storing an aluminum-containing feedstock, vessel **105** for storing acid, vessel **109** for storing water, and a vessel **406** for collecting hydrogen. In apparatus **200**: the vessels **150** of apparatus **100B** include a reaction vessel **206** and a furnace collection vessel **405**; heaters **111** of apparatus **100B** include a reaction vessel burner **154** for heating a reaction vessel **206** and a furnace burner **156** for heating furnace collection vessel **405**; and container **107** for collecting aluminum oxide from furnace collection vessel **405**.

[0039] Apparatus **200** also includes: a condenser **210**; a chiller **501**; a hydrogen transfer device **211**; an acid collection vessel **408**; a furnace collection vessel valve **399**; a separation device **401**; a separation medium **402** such as a filter paper; a furnace **155** including burner **156** for heating furnace collection vessel **405**; a first valve **213**; and a second valve **214**.

[0040] Apparatus **200** further includes pipes that connect the following components: vessel **103**, vessel **105**, and vessel **109** to reaction vessel **206**; reaction vessel **206** to condenser **210**, chiller **501**, hydrogen transfer device **211**, vessel **406**, and acid collection vessel **408**; and from reaction vessel **206** through furnace collection vessel valve **399** and separation device **401** to furnace collection vessel **405**. The flow of hydrogen from vessel **406** is controlled to burner **154** by first valve **213** and from vessel **406** to burner **156** by valve **214**.

[0041] FIG. 2 further shows, for illustrative purposes only, the flow of processed material as acid **104**, acid vapors **108**, steam **110**, hydrogen **112**, contaminants **116**, and chlorinated aluminum oxide solution **322**.

[0042] Apparatus **200** can be used for the reaction of a feedstock including aluminum that comprises contaminants other than aluminum or aluminum oxide, referred to herein and without limitation, as "scrap aluminum" **102** with acid **104**; for the generation of hydrogen **112**; for a purification of the chlorinated aluminum oxide solution **322**; for the regeneration and collection of the acid **104** through condensation of the steam **110** and acid vapors **108**; the collection and storage of the hydrogen using hydrogen collector **212** contained within vessel **406**; the use of the hydrogen **112** for heating purposes using burner **154** and the drying and heating of aluminum oxides **514** using a burner **156** in furnace **155**.

[0043] More specifically, in a first step in the operation of apparatus **200**, contaminated scrap aluminum **102** and acid **104** are combined in reaction vessel **206** to generate a chlorinated aluminum oxide solution **322**, hydrogen **112** and contaminants **116**, as shown, for

example in Block **15a** of FIG. 1A. More specifically, the products of reaction vessel **206** may include gaseous products, including but not limited to hydrogen, steam, and acid vapors, and non-gaseous products, including but not limited to aluminum-containing compounds, contaminants, water, and acid.

[0044] The hydrogen **112** of the gaseous products is then passed through condenser **210** and hydrogen transfer device **211** to hydrogen collector **212** contained within vessel **406**. Hydrogen **112** can be collected efficiently by compression with pressurized storage and by the absorption of the hydrogen by metal hydrides such as lanthanum nickel five ($LaNi_5$). This is a necessary step in this process if the hydrogen is to be used for other purposes or for heating within the process itself.

[0045] The heat of reaction of contaminated scrap aluminum **102** and acid **104** will cause the solution in reaction vessel **206** to increase in temperature and ultimately to reach a boiling point of about 120 ^{o}C. Steam and any acid vapors will flow through condenser **210** where they become liquids, and through hydrogen transfer device **211** for collection in acid collection vessel **408**.

[0046] A second step in the operation of apparatus **200** occurs when the reaction of contaminated scrap aluminum **102** and acid **104** in vessel **206** has gone to completion, or is nearly complete, as shown, for example in Block **15b** of FIG. 1A. At this point, the non-gaseous products of vessel 206, which may include but are not limited to reacted aluminum, water, acid, and possibly some contaminants, are provided to furnace collection vessel **405**. Thus, for example, at completion of the reaction of aluminum and acid, furnace collection vessel valve **399** may be opened, allowing chlorinated aluminum oxide solution **322** to pass through separation medium **402** within the separation device **401** and into furnace collection vessel **405**.

[0047] The separation medium **402** removes contaminants **116** from the chlorinated aluminum oxide solution **322**. The separation medium **402** would then be removed from the separation device **401** and the contaminants **116** discarded. The separation medium **402** would then be reinserted into separation device **401**. This step may provide a more purified final aluminum oxide product, and assists in both the removal of certain metal oxides as well as for the removal of non-metallic constituents, such as paper. As an example of this next step in the operation of apparatus **200**, Fig. 2 shows the purification of the chlorinated aluminum

oxide solution **322** from contaminants **116** using separation device **401**, separation medium **402** and furnace collection vessel **405**. The resulting chlorinated aluminum oxide solution **322** collects in the furnace collection vessel **405** after separating the solid and liquid phases.

[0048] The furnace **155** is then operated to heat chlorinated aluminum oxide solution **322** to dryness at temperatures of the order of 120 °C. The steam so generated would pass back through separation medium **402**, and reaction vessel **206,** and is then condensed at the condenser **210**. The water **120** so formed would then flow through the hydrogen transfer device **211** and into acid collection vessel **408**.

[0049] Acid **104** collected in acid collection vessel **408** may be returned as regenerated acid into vessel **105**.

[0050] As the chlorinated aluminum oxide solution **322** approaches a dry condition within furnace collection vessel **405** due to the heating by furnace **155**, the temperature within the furnace collection vessel **405** increases to temperatures, for example, between 400 °C and 1500 °C, or between 1000 °C and 1500 °C, or may be for example and without limitation, approximately 1200 °C. During this heating process acid vapors **108** will be evolved and travel with the steam **110** and hydrogen **112** to condenser **210** where the acid vapors will condense with the steam and form acid **104**. The acid **104** will flow through hydrogen transfer device **211** into the acid collection vessel **408**, thereby providing regenerated acid for future use. Alpha phase aluminum oxide **614** is also obtained from this high temperature heating and is removed from the furnace collection vessel **405**.

[0051] Figures 3 and 4 show the drying and heating process steps of apparatus **200**, and is generally similar to apparatus **100B**, except as explicitly stated.

[0052] FIG. 3 shows the steps for regeneration of acid as the purified solution is heated to dryness. Apparatus **200** may be operated similarly to collect chlorinated aluminum oxide solution **322** in furnace collection vessel **405** as described previously. As shown in FIG. 3, apparatus **200** provides hydrogen from hydrogen collection vessel **406** via furnace hydrogen valve **214** to a furnace burner **156**. More specifically, furnace collection vessel **405**, which contains chlorinated aluminum oxide solution **322**, is heated by furnace **154** using previously generated hydrogen **112**. The hydrogen is provided from hydrogen collector **212** contained within vessel **406** to fuel furnace burner **156** to generate steam **110** and acid vapors **108** that are thereafter condensed using chiller **501** and condenser **210** and collected in acid collection

vessel **408**. The heat is used to dry the chlorinated aluminum oxide solution **322**, and then heat the resulting solids to sufficient temperature to drive out the steam **110** and acid vapors **108** that may still be contained within the solids. Temperatures from of order 100 °C to 400 °C are required for this step and are attained as furnace **155** is ramped to temperatures, for example, between 100 °C and 500 °C, or between 400 °C and 500 °C, or may be for example and without limitation, approximately 400 °C. This is advantageous because significant heat is required to boil off the water in the solution and the heat generated by the collection and burning of hydrogen reduces the need for external energy.

[0053] FIG. 4 highlights the use of apparatus **200** as used for heating dried aluminum oxide to produce alpha phase aluminum oxide **614**. As shown in FIG. 4, apparatus **200** may also be used for the heating of dried aluminum oxide **514** in furnace collection vessel **405** to produce alpha phase aluminum oxide **614** by using furnace **155**. This step is important to produce the phase transformation of the dried aluminum oxide **514** to alpha phase aluminum oxide **614** that has the purity, hardness or refractory characteristics desired from fused aluminum oxides. The temperature for this step may be, for example, between 400 °C and 1500 °C, or between 1000 °C and 1500 °C, or may be for example and without limitation, approximately 1200 °C.

[0054] A furnace **155** is one particular means to provide the heating required, but other heating methods are also applicable – especially those heating devices that can use the hydrogen being generated. A significant amount of hydrogen is generated by method 10, and this can provide most or all of the heat needed to reach the stated temperatures.

[0055] Figures 6 and 7 are more detailed schematics of another embodiment of an apparatus **600** that is generally similar to the embodiment of FIG. 1B. As shown in FIG. 6, apparatus **600** includes an aluminum insertion device **802**, a hydrogen output **812**, a cooling coil **814** and a cooling water flow control subsystem **816**. Apparatus **600** is similar to apparatus **100**, except as discussed subsequently.

[0056] Apparatus **600** is configured to generate more hydrogen and a dried aluminum oxide, rather than the aluminum oxide product of apparatus **100A**, so as to reduce the energy requirements of the process. In apparatus **600**, the heating of the chlorinated aluminum oxide solution **322** may be performed using only internal heating and other energy sources so as to maximize hydrogen output **812**. This process is simpler than some of the other apparatus

embodiments discussed herein, but still provides a hydrogen output **812** from contaminated scrap aluminum **102** using a reaction with acid **104**. Regeneration of acid is provided, so that the only feedstock required once this process is started are additional contaminated scrap aluminum **102**.

[0057] Specifically, apparatus **600** may be used to react contaminated scrap aluminum **102** with acid **104** in reaction vessel **206** through the use of an aluminum insertion device **802** that provides a means to lower the contaminated scrap aluminum **102** into the solution. The reaction vessel **206** contains the acid **104** into which the contaminated scrap aluminum **102** is inserted. A cooling coil **814** is included in this embodiment to help control the temperature of the reacting solution so that it does not boil. Cooling water flow control subsystem **816** controls the flow rate of room temperature water through the cooling coil **814**. Heating device **819** is connected to reaction vessel **206** to provide additional heating if necessary. Chiller **501** and condenser **210** are used to condense any significant water and acid vapors **108** and return them to the acid **104** and chlorinated aluminum oxide solution **322**. Hydrogen **112** is generated and exits the system through hydrogen output **812**.

[0058] The chlorinated aluminum oxide solution **322** generated by apparatus **600** may be removed via an exhaust valve (not shown) connected to the bottom of the reaction vessel **206** and then with the use of the portion of apparatus **600** shown in FIG. 7, acid **104** can be regenerated and the dried aluminum oxide **514** produced by drying the chlorinated aluminum oxide solution **322** by heating the solution to dryness within furnace collection vessel **405**. Temperatures from of order 100 °C to 400 °C are required for this step and are attained as furnace **155** is ramped to temperatures, for example, between 100 °C and 500 °C, or between 400 °C and 500 °C, or may be for example and without limitation, approximately 400 °C. As described previously, the acid vapors **108** and steam **110** are condensed in condenser **210** and collected in acid collection vessel **408**. Aluminum oxide **514** is obtained from furnace collection vessel **405**.

[0059] Alternatively, the entire reaction vessel **206** of apparatus **200** can be placed in furnace **155** and the chlorinated aluminum oxide solution **322** heated to regenerate the acid **104** and obtain dried aluminum oxide **514**.

[0060] Another alternative step of method **10** is the separation of aluminum oxide. Figure 5 illustrates the purification of the alpha phase aluminum oxide of any magnetic components

that may be used in any one of apparatus **100A**, **100B**, **100C**, **200**, or **600**. Furnace collection vessel **405** is shown as including using a magnet **702**. Contaminants **116** may include, for example, magnetic particles **701**, such as some metal oxides. Aluminum oxide is not magnetic whereas other metal oxides such as iron oxide are magnetic. The use of magnet **702** provides additional purification via magnetic means. Thus, for example, magnet **702** may be inserted onto furnace collection vessel **405** to collect, and then remove such particles to produce a purified aluminum oxide **714**.

ALTERNATIVE EMBODIMENTS

[0061] Several alternative embodiments are directly applicable to the embodiments presented above. While the above description has many specifics, it should be construed as one of several potential configurations and arrangements of components. Furthermore, several of the steps described so far can be removed from method **10** without dramatically affecting the results. For example, the filtering of the chlorinated aluminum oxide solution **322** to remove contaminants **116** may not be necessary dependent upon the requirements of the specific process and device. Similarly the final magnetic purification may not be needed. The minimum requirements of this process and device are that hydrogen **112** is generated through the reaction of at least aluminum and a byproduct from the reaction is processed to provide a material of greater purity than the starting contaminated scrap aluminum **102**.

[0062] Other alternative embodiments should be recognized. The heating of solutions and solids does not necessarily need to use the burning of the hydrogen **112** generated by method **10**. Any other standard heating methods can also be employed. Steam **110** could be used to generate useful forms of work, as in apparatus **100C**. Since no process is 100% cyclic without some input of minimally lost reactants, some additional hydrochloric acid **104** may need to be added occasionally to provide for small loses resulting during the hydrochloric acid regeneration process.

[0063] Furthermore, a number of alternative embodiments and the associated ramifications of these embodiments can be envisioned. For instance, the size of the apparatus to execute method 10 can be scaled all the way from the laboratory level to full scale plant operations. Furthermore, the form of the aluminum containing mixtures can range from powders to gross mixtures of varying metal components along with other non-metallic and organic components such as steel, paper and petroleum based organics. The aluminum mixtures can range all the way from pure aluminum to mixtures of aluminum, other metals,

inorganics and organics. Aluminum can be mixed with other metals such as iron as in irony aluminum. Aluminum can be backed with paper to form paperbacked aluminum. Aluminum turnings can be mixed with water based and organic cutting solutions. These are just a few instances of mixtures that can be processed by the claimed processes and devices. Of particular note is the many forms of scrap aluminum: old mixed scrap aluminum, utensil aluminum scrap, aluminum turnings, scrap aluminum extrusions, scrap low copper aluminum, scrap litho sheets, scrap cast aluminum, scrap clean painted aluminum, painted aluminum insulated scrap, scrap coated aluminum, used beverage cans (loose), shredded used beverage cans, baled used beverage cans, briquetted used beverage cans, new beverage can stock scrap, remelt aluminum ingot, remelt aluminum sows, scrap mixed irony aluminum, scrap low grade irony aluminum, scrap auto transmissions, scrap aluminum auto rads, scrap insulated aluminum wire, scrap supported aluminum cable, scrap bare aluminum wire, scrap aluminum auto wheels, aluminum nodules, scrap aluminum foil, scrap paperbacked aluminum foil and aluminum auto fragments.

[0064] In addition, there are various means to purify solids, liquids and gases that can be included in apparatus for performing method **10**. Adsorptive filtration as used in carbon traps, absorptive filtration as used in ion exchange filtration and metal hydride absorption and desorption should all be included as tools of the trade for separation and purification purposes. Mechanical separation techniques such as sorting, gravity based methods such as decanting, magnetic separation as well as other means to separate different phases from each other should be included as tools to achieve a particular process based upon this process. In particular, the magnetic separation of FIG. 5 could be performed at other points within the process such as after the dried aluminum oxide is prepared and before the dried aluminum oxide is heated or calcined. Filtration using both porous and filtering medium, centrifugal methods such as cyclone filtration, distillation methods such as condensation distillation, solubility differentiation methods such as precipitation filtration and electrochemical separation by reducing and oxidizing out of solution specific components such as in the plating of metals should be included as methods that are within the scope of method **10** as long as they contribute to the basic requirements of this process.

[0065] Acids which may be used may include hydrochloric acid, sulfuric acid, nitric acid and mixtures thereof. Other condensation methods such as cooling baths and the passing of heated vapors through water and mineral acid mixtures should be included as alternative

methods to achieve the condensation of steam and acid vapors. In addition, low temperature gas and liquid phase cooling (such as liquid nitrogen and liquid nitrogen vapors) along with ice and other solid phase cooling (such as solid carbon dioxide) should be within the scope of method **10** as well as any standard methods known in the art that are used to cool heated vapors.

[0066] Different methods for the collection and storage of hydrogen may include the use of metal hydrides and the compression of hydrogen in pressurized storage tanks. These are the two main storage methods, but others exist that are applicable to performing the steps of method **10**.

[0067] Other heat generating devices should be included such as using fuel combustion, hot plates, ovens, furnaces, microwave heating and microwave induction methods and any other means that impinges or causes heat to be generated within a process or device. In addition, other reactive regeneration methods such as gas phase product separation as is used in the high temperature heating of aluminum chloride hexahydrate should be within the scope of the present invention. Additionally, aluminum purification through aluminum production via electrolytic means is within the scope of the present invention, as long as one of the starting materials for aluminum production results from this process and device.

[0068] Accordingly, the scope of the present invention should not be determined by the embodiments illustrated, but by the breadth of the embodiments, the appended claims and their logical extensions.

EXAMPLES

[0069] The operation of method **10** will now be discussed, without limitation, with reference to the Figures. Apparatus **100A** provides what is likely the most basic process for the several embodiments described. The primary minimal requirements of this process and device are that hydrogen **112** is generated through the reaction of contaminated scrap aluminum **102** with acid **104** and a byproduct containing aluminum from the reaction is processed to provide aluminum oxide **114**. This process and device are especially suited to the use of contaminated scrap aluminum **102** with hydrochloric acid because of the reactions utilized, the ability to regenerate the hydrochloric acid and the purification methods utilized.

[0070] The following experiments and chemical analysis of products were obtained by a

laboratory scale version of apparatus **100A**. Type 4032 aluminum was used for these experiments with a composition as shown in Table 1 as determined by an external laboratory (West Penn Testing Group). A 12.05 gram sample of 4032 aluminum was reacted with 248 ml of 18.5 wt. % hydrochloric acid to completion. The resulting solution with both a solid phase of contaminants and a solution of chlorinated aluminum oxide was then decanted into two samples – one containing an excess of the solution with limited contaminants (the decanted solution) and one containing an excess of the solid residue (the residue solution). The residue solution was heated to dryness at temperatures up to 190 °C and then transferred to a furnace **155** and heated for four hours at temperatures up to 402 °C. Final weight of residue sample was 6.99 grams. The decanted solution was heated to dryness at temperatures up to 116 °C and then transferred to furnace **155** and heated for four hours at temperatures up to 391 °C. Final weight of decanted sample was 15.99 grams. The decanted 391 °C calcined sample was analyzed by West Penn Testing Group. Specifically, the sample was heated to a temperature of 950 °C over a period of four hours. The compositional analysis of this 950 °C calcined sample is shown both with respect to oxides and elements in Table 1. Of significance is the observation that appreciable SiO_2 was removed by the decanting operation with a consequent improvement in the purity of the aluminum oxide **114** obtained.

Table 1. Aluminum and Aluminum Oxide Analyses

	Aluminum Metal Analysis		Oxide Analysis		Elemental Analysis
wt. %	Type 4032 Al	wt. %	From Decanted Solution	wt. %	From Decanted Solution
Si	12.46	SiO_2	5.40	Si	4.764
Fe	0.31	Fe_2O_3	0.16	Fe	0.208
Cu	0.93	CuO	0.35	Cu	0.529
Mn	0.021	MnO	0.012	Mn	0.017
Mg	1.21	MgO	1.09	Mg	1.242
Ni	0.79	NiO	0.46	Ni	0.681
Zn	0.023	ZnO	0.007	Zn	0.011
Ti	0.042	TiO_2	0.027	Ti	0.030
Sr	0.019	SrO	0.008	Sr	0.013
Al	84.165	Al_2O_3	92.43	Al	92.504

[0071] In another experiment 10.85 grams of 6063 type aluminum was reacted with 248 ml of 18.5 wt. % hydrochloric acid 104. The resulting solution with both a solid phase of

contaminants and a solution of chlorinated aluminum oxide was decanted into two samples – one containing an excess of the solution with limited contaminants (the decanted solution) and one containing an excess of the solid residue (the residue solution). The residue solution was heated to dryness at temperatures up to 164 °C and then transferred to a furnace **155** and heated for four hours at temperatures of order 401 °C. Final weight of residue sample was 7.39 grams. The decanted solution was heated to dryness at temperatures up to 145 °C and then transferred to a furnace **155** and heated for four hours at temperatures of order 395 °C. Final weight of decanted sample was 15.14 grams. A portion of this powdered decanted sample was sent to Washington Mills for calcining at 1300 °C for one hour. X-ray diffraction was performed on this calcined aluminum oxide sample. The Washington Mills analysis of the x-ray diffraction pattern showed that the 1300 °C calcined sample was 95 to 97.7% alpha phase aluminum oxide (corundum). According to Washington Mills this was a very pure sample with only a small amount of secondary phases (2.3 to 5%) and no more than 1.75% amorphous phase.

[0072] The generation of hydrogen is best illustrated with the following experiment that used the apparatus described in Figs. 6 and 7. In one experiment, 1085 grams of 6063 type aluminum reacted with 22.7 liters of 18.5 wt. % hydrochloric acid. After reaction went to completion there was 396 grams of aluminum remaining and 892 liters of hydrogen collected. A 296 gram sample of the solution resulting from the reaction was heated to dryness at temperatures up to 136 °C and then 86% of the sample was transferred to a furnace and heated for four hours at temperatures of order 400 °C. Final weight of powder residue sample was 15.54 grams. By both gravimetric means and West Penn Testing Group analysis, samples calcined at temperatures of order 400 °C for four hours have a residual chlorine content of from 9 to 14 wt.%. Using these results it is found that the reaction process for this case generated approximately 96% of the maximum theoretical hydrogen and approximately 99% of the maximum theoretical dried aluminum oxide.

[0073] Reference throughout this specification to "one embodiment," "an embodiment," or "certain embodiments" means that a particular feature, structure or characteristic described in connection with the embodiment is included in at least one embodiment of the present invention. Thus, appearances of the phrases "in one embodiment," "in an embodiment," or "in certain embodiments" in various places throughout this specification are not necessarily all referring to the same embodiment. Furthermore, the particular features, structures or

characteristics may be combined in any suitable manner, as would be apparent to one of ordinary skill in the art from this disclosure, in one or more embodiments.

[0074] It is thus to be understood that the invention includes all of the different combinations embodied herein. Throughout this specification, the term "comprising" shall be synonymous with "including," "containing," or "characterized by," is inclusive or open-ended and does not exclude additional, unrecited elements or method steps. "Comprising" is a term of art which means that the named elements are essential, but other elements may be added and still form a construct within the scope of the statement. "Comprising" leaves open for the inclusion of unspecified ingredients even in major amounts.

[0075] Similarly, it should be appreciated that in the above description of exemplary embodiments of the invention, various features of the invention are sometimes grouped together in a single embodiment, figure, or description thereof for the purpose of streamlining the disclosure and aiding in the understanding of one or more of the various inventive aspects. This method of disclosure, however, is not to be interpreted as reflecting an intention that the claimed invention requires more features than are expressly recited in each claim. Rather, as the following claims reflect, inventive aspects lie in less than all features of a single foregoing disclosed embodiment. Thus, the claims following the detailed description are hereby expressly incorporated into this detailed description, with each claim standing on its own as a separate embodiment of this invention.

[0076] Thus, while there has been described what is believed to be the preferred embodiments of the invention, those skilled in the art will recognize that other and further modifications may be made thereto without departing from the spirit of the invention, and it is intended to claim all such changes and modifications as fall within the scope of the invention. Steps may be added or deleted to methods described within the scope of the present invention.

CLAIMS

1. A method for producing hydrogen and aluminum oxide from aluminum and contaminants, said method comprising:

accepting a feedstock including aluminum and contaminants;

reacting the accepted feedstock with an acid to produce hydrogen and other products of reaction;

forming aluminum oxide from the other products of reaction;

collecting the aluminum oxide; and

performing one or more of

collecting the hydrogen, and

generating heat from the chemical energy in the hydrogen, where the generated heat is provided to assist in one or more of:

said reacting the accepted feedstock with acid and

said forming aluminum oxide.

2. The method of Claim 1, further comprising:

recovering regenerated acid from one or more of said reacting the accepted feedstock and said forming aluminum oxide; and

providing the regenerated acid as the acid for said reacting the feedstock and acid.

3. The method of Claim 1 wherein the acid is hydrochloric acid.

4. The method of Claim 1 wherein the acid includes chlorine, where the other products of reaction include a chlorinated aluminum oxide solution, and where said forming aluminum oxide includes heating the chlorinated aluminum oxide solution to a temperature equal to or greater than 400 °C.

5. The method of Claim 4 further including:

purifying the chlorinated aluminum oxide solution by filtration.

6. The method of Claim 1, wherein said forming aluminum oxide includes separating contaminants from the feedstock, said other products of reaction.

7. The method of Claim 1 further including:

purifying the aluminum oxide.

8. The method of Claim 1 further including:

drying the aluminum oxide; and

removing contaminants from the dried aluminum oxide with a magnet.

9. The method of Claim 1, where said aluminum oxide is alpha phase aluminum oxide.

10. A method for producing hydrogen and aluminum oxides from aluminum with a regenerated acid, said method comprising:

accepting a feedstock including aluminum and/or aluminum oxide;

reacting the accepted feedstock with an acid to produce hydrogen and other products of reaction;

forming aluminum oxide from the other products of reaction;

collecting the aluminum oxide;

performing one or more of

collecting the hydrogen, and

generating heat from the chemical energy in the hydrogen, where the generated heat is provided to assist in one or more of:

said reacting the accepted feedstock with acid and

said forming aluminum oxide;

recovering regenerated acid from one or more of said reacting the accepted feedstock and said forming aluminum; and

providing the regenerated acid as the acid for said reacting the feedstock and acid.

11. The method of Claim 10, wherein the acid is hydrochloric acid.

12. The method of Claim 10, wherein the acid includes chlorine, where the other products of reaction include a chlorinated aluminum oxide solution, and where said forming aluminum oxide includes heating the chlorinated aluminum oxide solution to a temperature equal to or greater than 400 °C.

13. The method of Claim 12, further including:

purifying the chlorinated aluminum oxide solution by filtration.

14. The method of Claim 12, further including:

purifying the aluminum oxide.

15. The method of Claim 12, further including:

drying the aluminum oxide; and

removing contaminants from the dried aluminum oxide with a magnet.

16. The method of Claim 10, where said aluminum oxide is alpha phase aluminum oxide.

17. A device for producing hydrogen and aluminum oxides from a feedstock including aluminum and/or aluminum oxide and an acid, said device comprising:

a reaction vessel adapted to accept the feedstock and the acid and produce first gaseous products including hydrogen and non-gaseous products;

a first heater for heating the reaction vessel;

furnace collection vessel to accept the non-gaseous products and produce aluminum oxide and second gaseous products;

a second heater for heating the furnace collection vessel; and

a gas collection device to accept one or more of the first gaseous products and the second gaseous products; and

an acid regeneration system to recover acid from said gas collection device and provide the regenerated acid to the reaction vessel;

such that hydrogen and aluminum oxide may be produced using a regenerated acid.

18. The device of Claim 17, further including a separation device to remove contaminants from the feedstock.

19. The device of Claim 17 where the first heater and/or the second heater generates heat from the chemical energy of the produced hydrogen.

20. The device of Claim 17, where said acid is a chlorine-containing acid, where the non-gaseous products include a chlorinated aluminum oxide solution, and where the second heater heats the furnace collection vessel to a temperature equal to or greater than 400 °C.

21. The device of Claim 17, further including a filter to remove contaminants from the non-gaseous products.

22. The device of Claim 17, further including a magnet to remove magnetic contaminants from the furnace collection vessel.

23. A device substantially as shown and described.

24. A method substantially as shown and described.

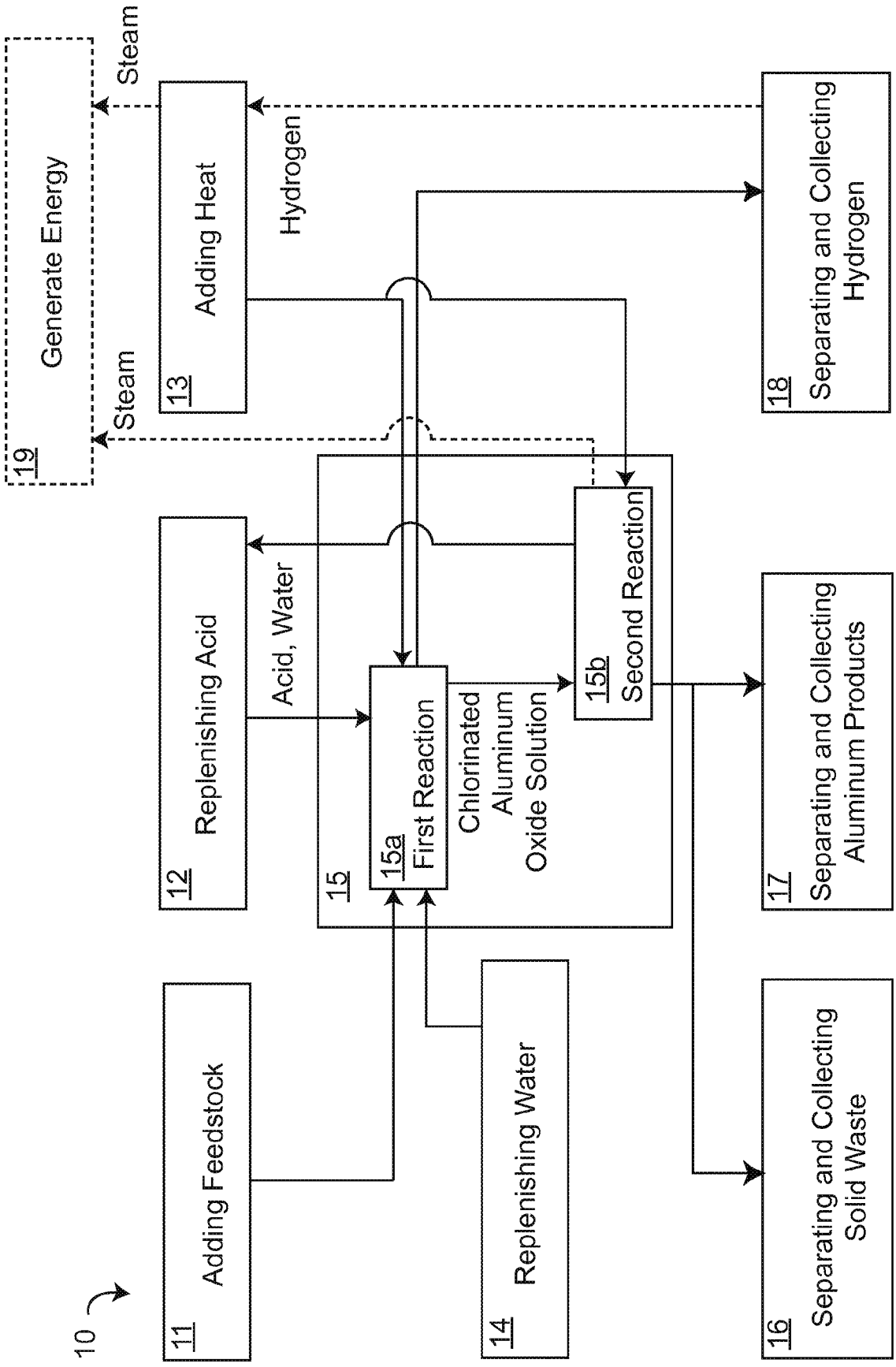

10
11 Adding Feedstock
12 Replenishing Acid
13 Adding Heat
14 Replenishing Water
15
15a First Reaction
15b Second Reaction
16 Separating and Collecting Solid Waste
17 Separating and Collecting Aluminum Products
18 Separating and Collecting Hydrogen
19 Generate Energy
Acid, Water
Chlorinated Aluminum Oxide Solution
Hydrogen
Steam
Steam

FIG. 1A

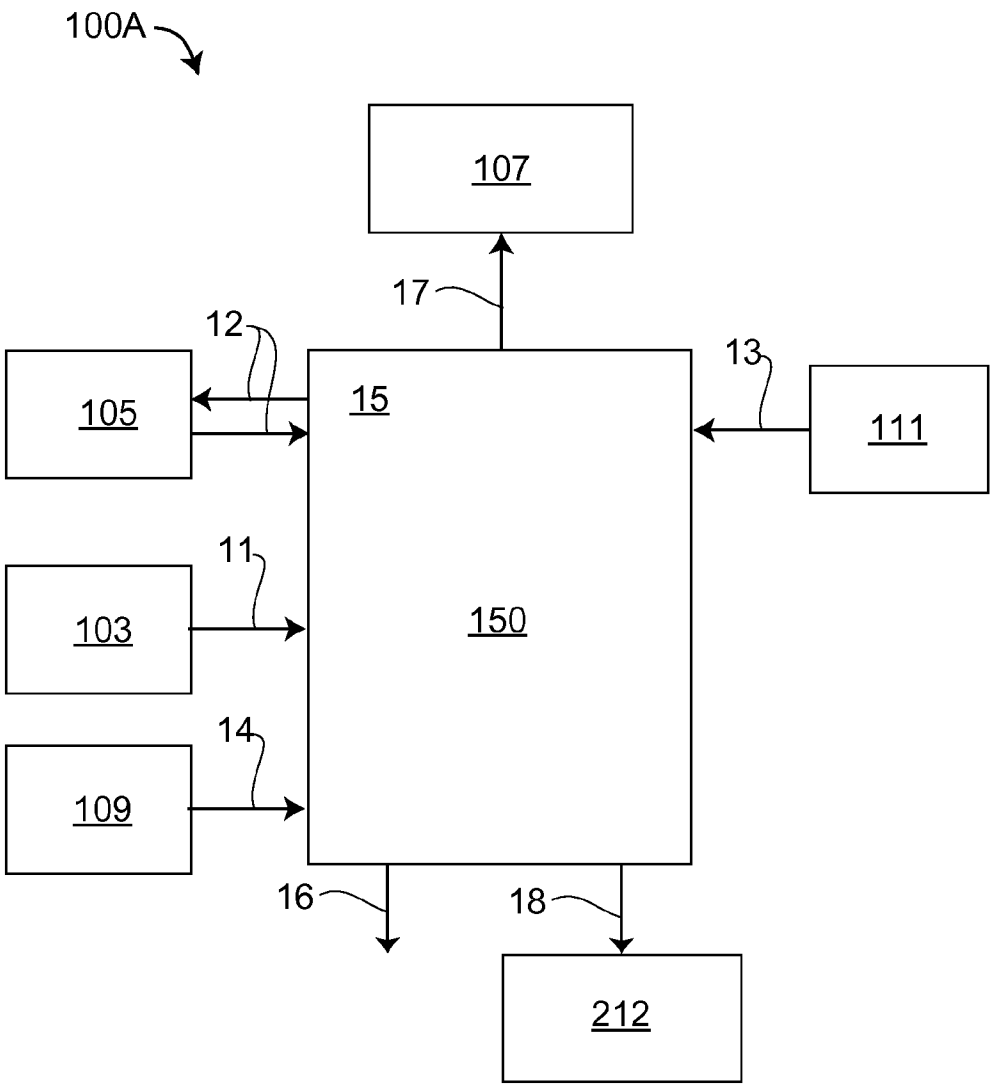


Fig. 1B

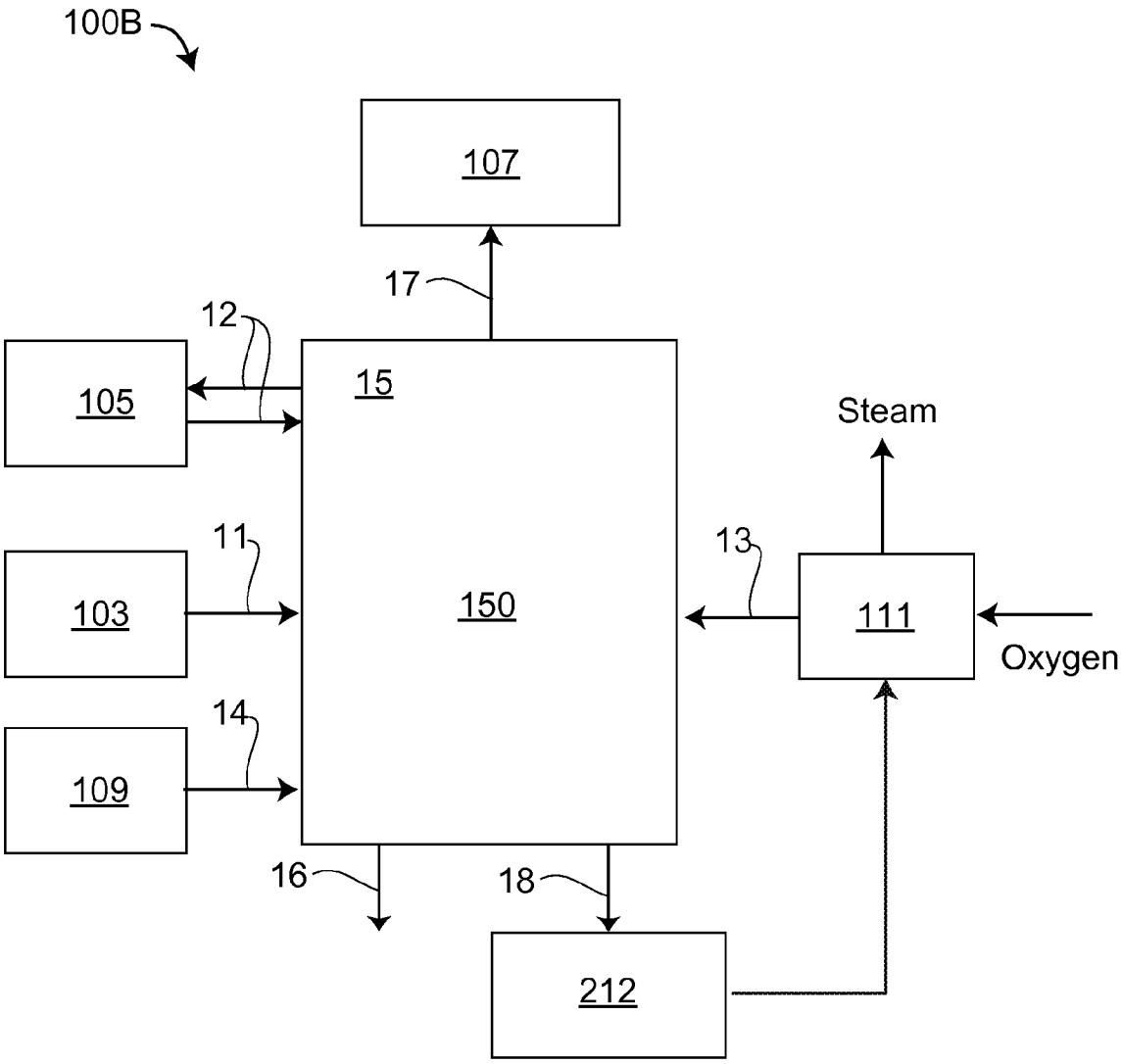

100B
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Fig. 1C

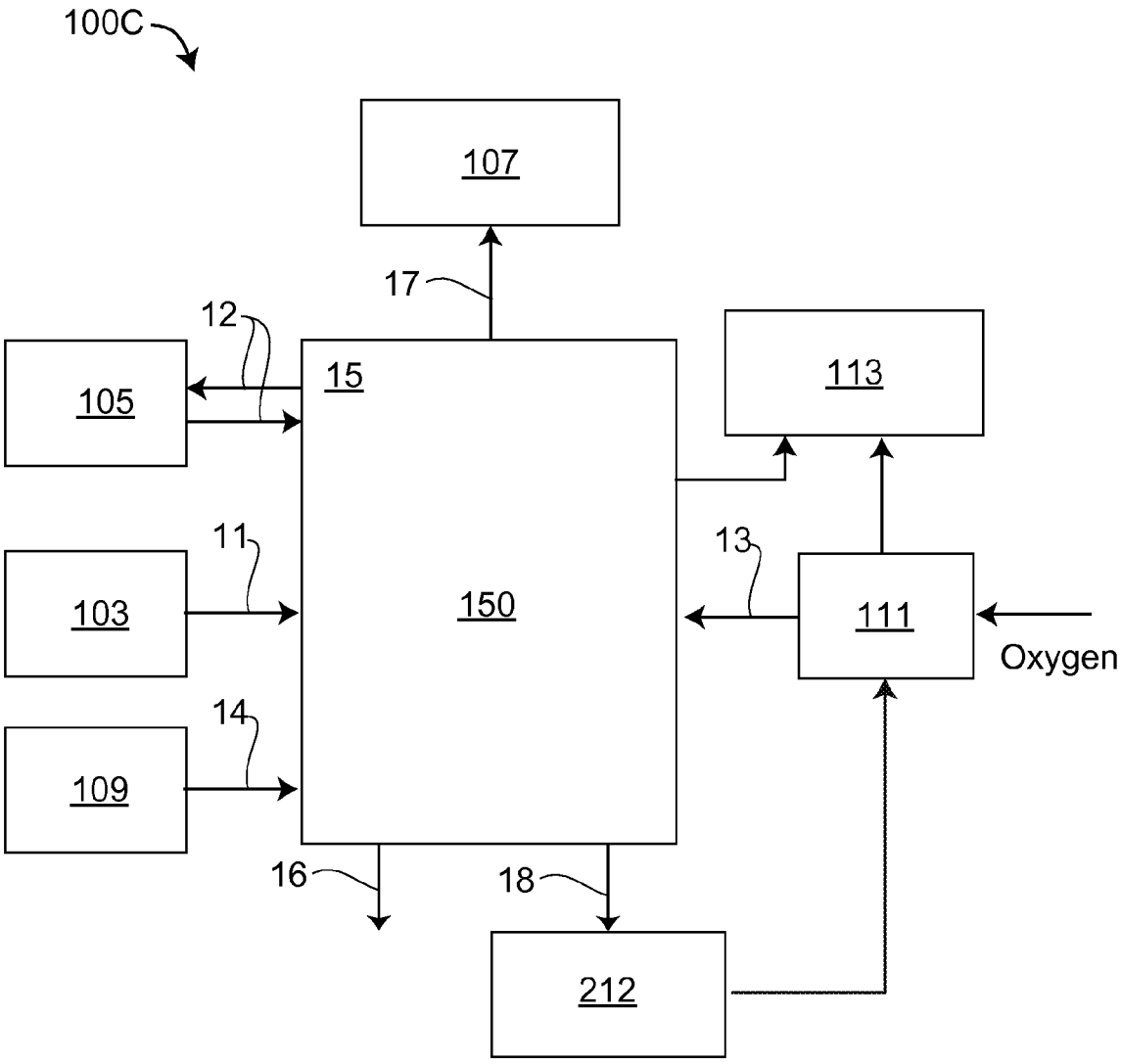

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Fig. 1C

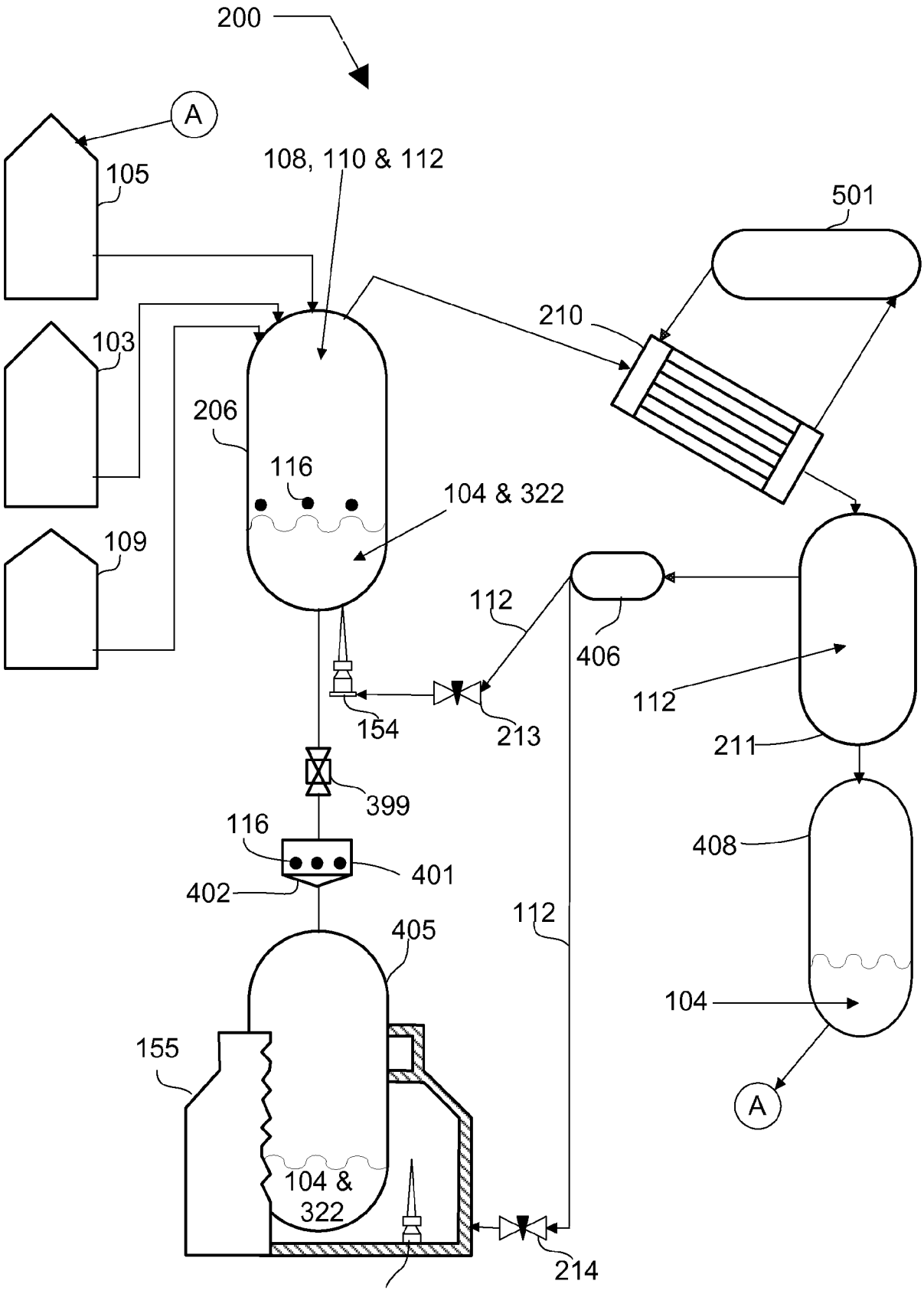

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FIG. 2

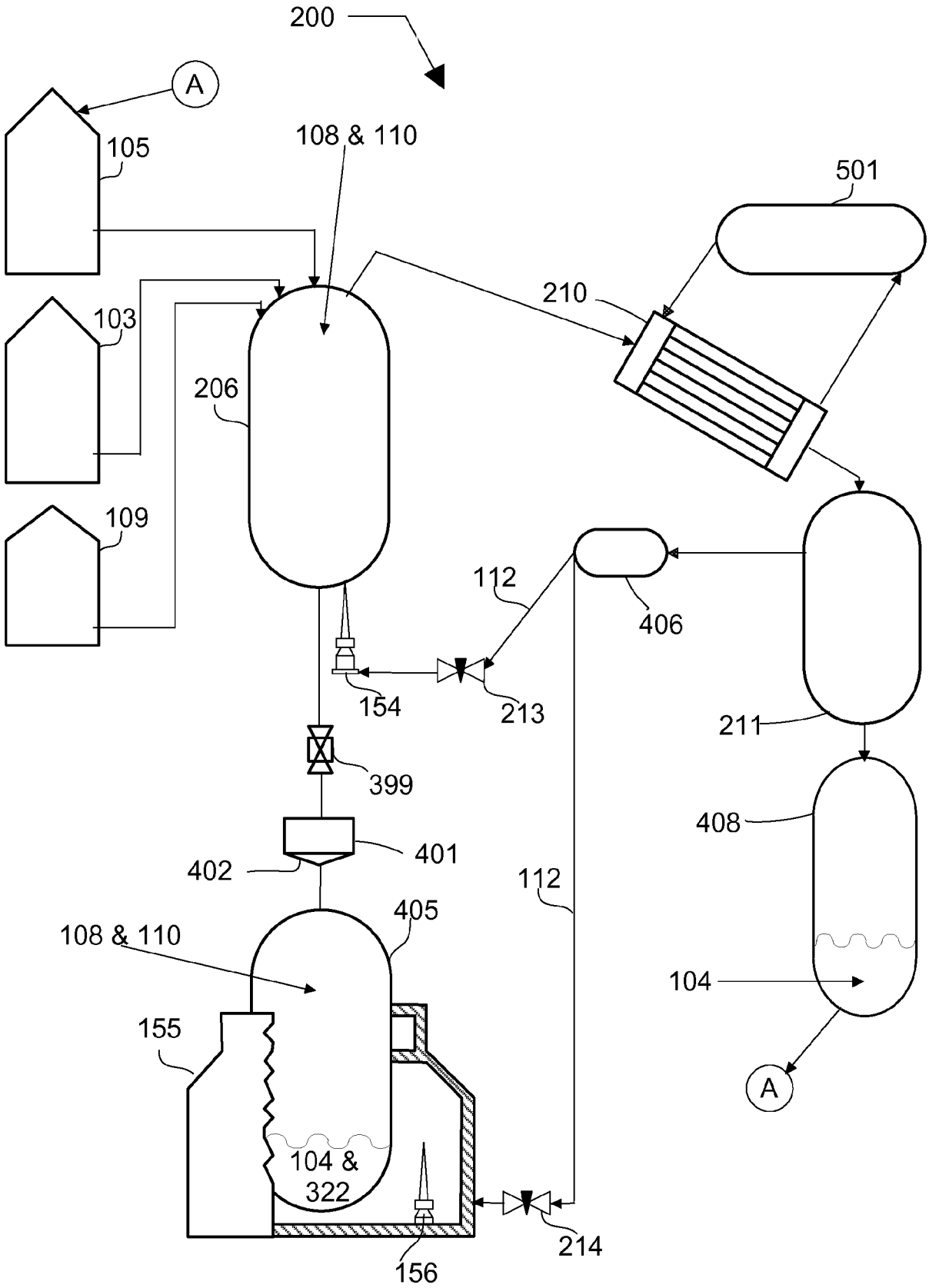

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FIG. 3

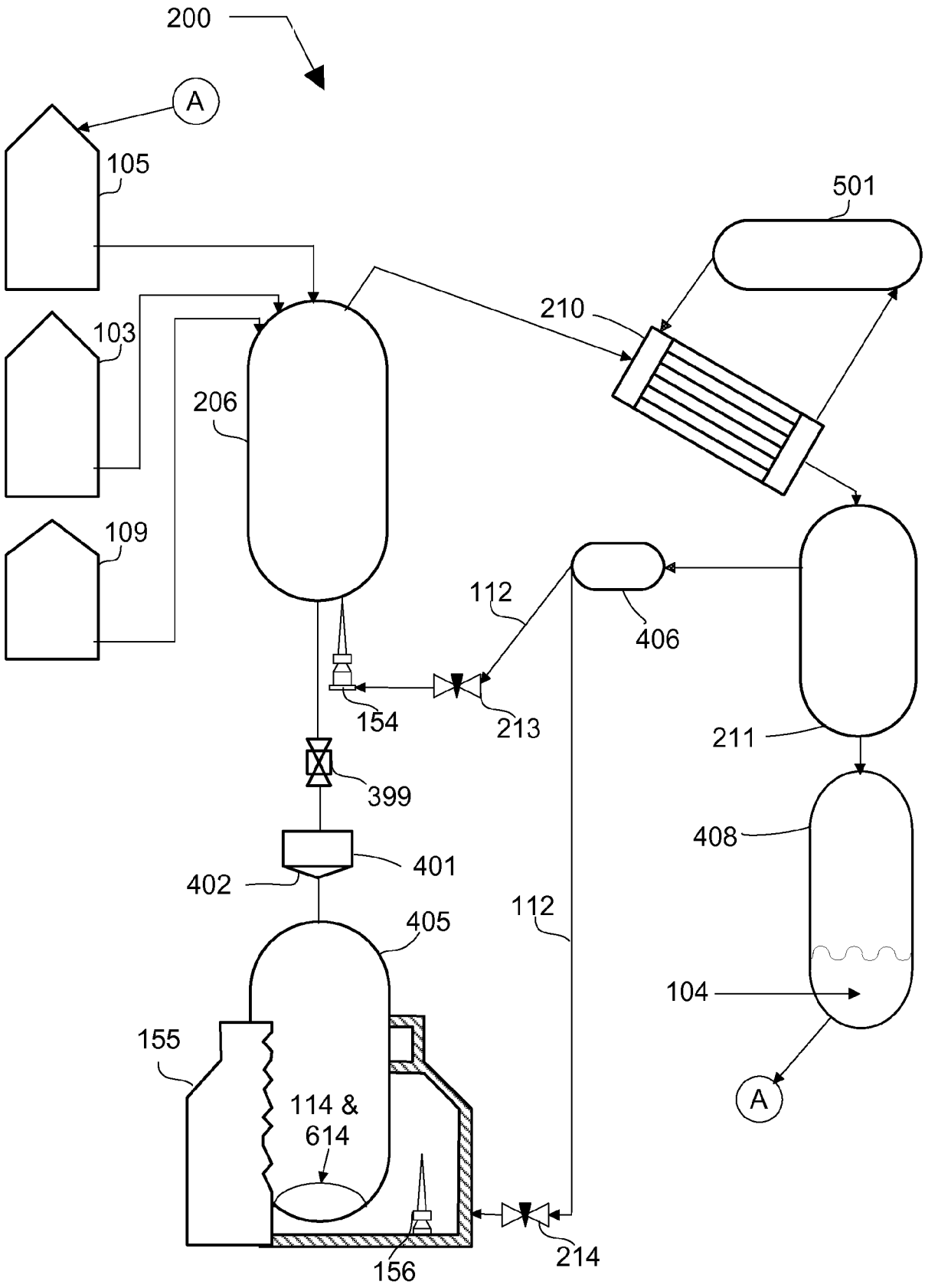

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FIG. 4

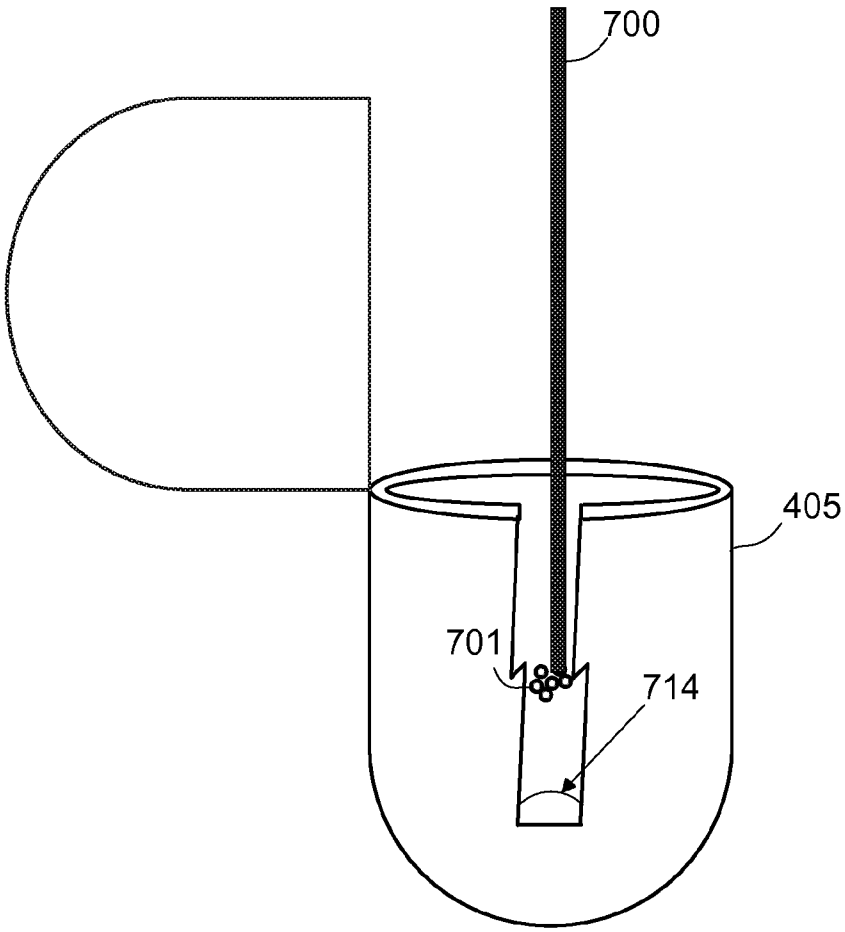


FIG. 5

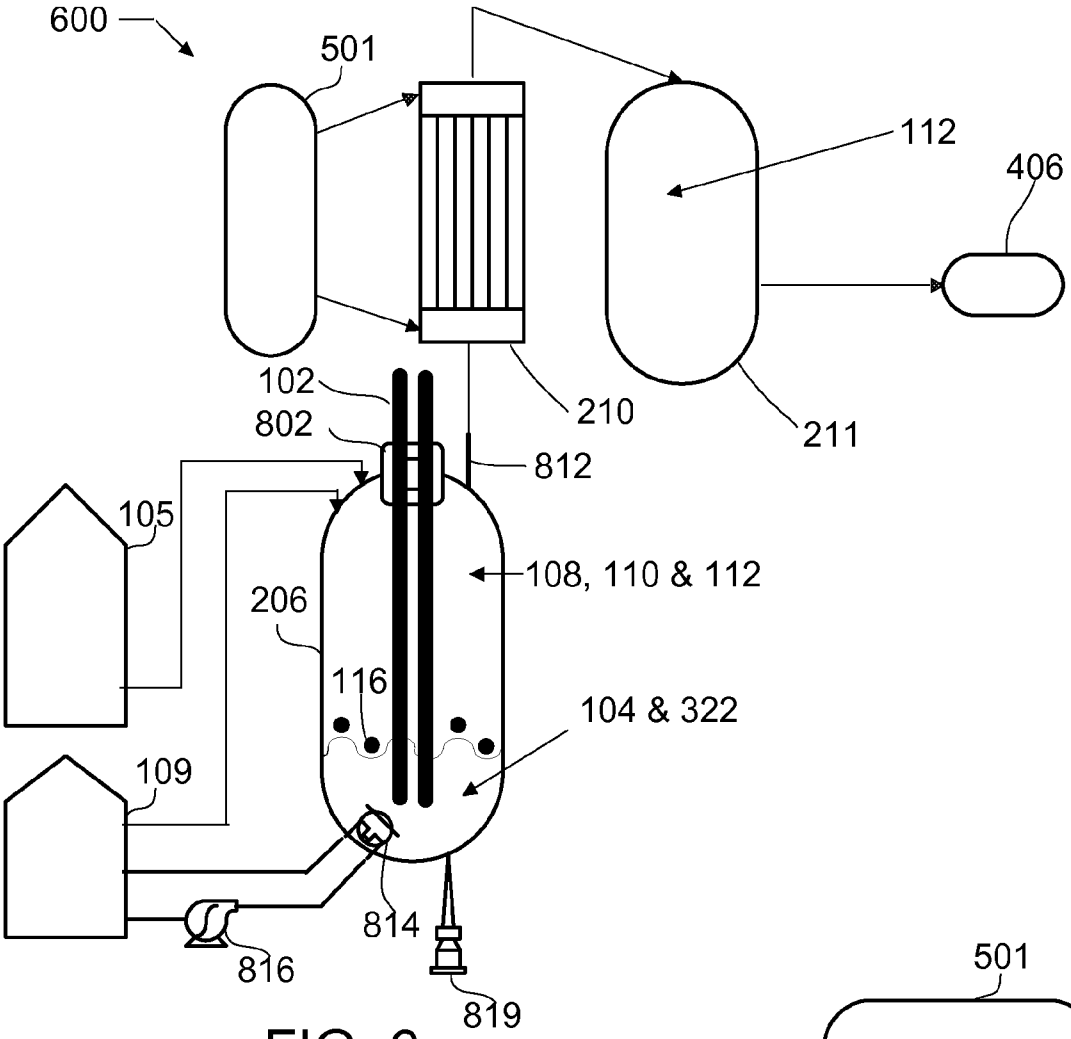

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FIG. 6

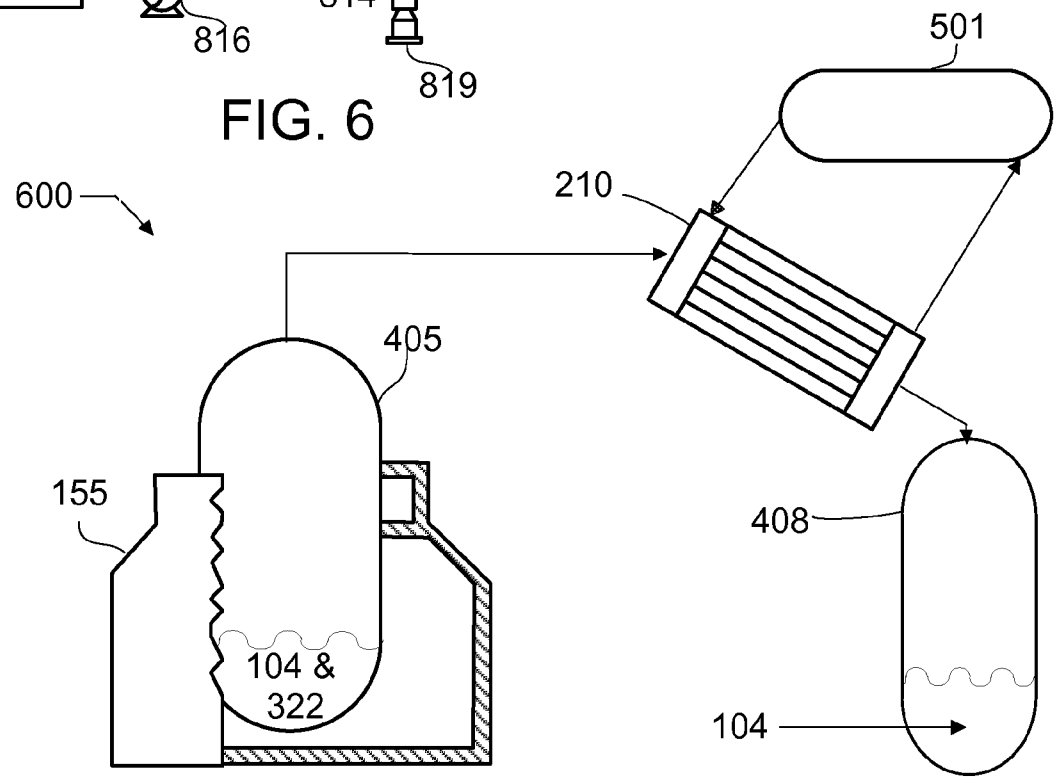

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FIG. 7

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/049146

A. CLASSIFICATION OF SUBJECT MATTER

C01B 3/02(2006.01)i, C01F 7/02(2006.01)i, B01J 19/24(2006.01)i

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)
C01B 3/02; C01B 3/08; C01F 7/20; C01F 7/22; C01F 7/26; B01D 9/02; C01F 7/30; C01F 7/02; B01J 19/24

Documentation 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 models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: aluminium oxide, hydrogen, acid, heat, chlorinated aluminum oxide

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4486402 A (GURTNER, BERNARD et al.) 04 December 1984 See abstract; column 3, lines 41-65; column 6, lines 30-63; claims 1, 14.	1-22
A	US 2005-0276747 A1 (TANAKA, YOSHIROU et al.) 15 December 2005 See abstract; paragraphs [0020], [0024]; claims 1-2; figure 1.	1-22
A	US 4110399 A (GAUDERNACK BJORN et al.) 29 August 1978 See abstract; claims 1, 3, 11, 12.	1-22
A	JP 05-330820 A (NITTETSU KAKOKI KK et al.) 14 December 1993 See abstract; paragraphs [0004], [0016], [0026].	1-22
A	US 4158042 A (DEUTSCHMAN, JOHN E.) 12 June 1979 See abstract; column 2, lines 31-57; claims 1, 7.	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 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	Date of mailing of the international search report
27 September 2013 (27.09.2013)	**27 September 2013 (27.09.2013)**

Name and mailing address of the ISA/KR
Korean Intellectual Property Office
189 Cheongsa-ro, Seo-gu, Daejeon Metropolitan City, 302-701, Republic of Korea
Facsimile No. +82-42-472-7140

Authorized officer
KIM Dong Seok
Telephone No. +82-42-481-8647

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/049146

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 23-24
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
It is not possible to clearly define the subject matter for claims 23-24 since they are worded as 'substantially as shown and described'.

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required addtional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/US2013/049146

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		SE 432923 C	09/08/1984
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