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(71) Applicant: **ORBITE ALUMINAE INC.** [CA/CA]; 6505 route Transcanadienne, Bureau 610, Saint-Laurent, Québec H4T 1S3 (CA).

(72) Inventors: **BOUDREAULT, Richard**; 2723 Luce-Guilbeault, Saint-Laurent, Québec H4R 2T3 (CA). **FOURNIER, Joel**; 1761 des Amarantes, Carignan, Québec J3L 4Z8 (CA). **PRIMEAU, Denis**; 2166 Place de l'Eglise, Ste-Julie, Québec J3E 2G5 (CA). **LABRECQUE-GILBERT, Marie-Maxime**; 4599 Beauchesne, Laval, Québec H7T 2T6 (CA).

(74) Agent: **BERESKIN & PARR LLP/S.E.N.C.R.L., S.R.L.**; 40th Floor, 40 King Street West, Scotia Plaza, Toronto, Ontario M5H 3Y2 (CA).

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# (54) Title: PROCESSES FOR PREPARING ALUMINA AND VARIOUS OTHER PRODUCTS

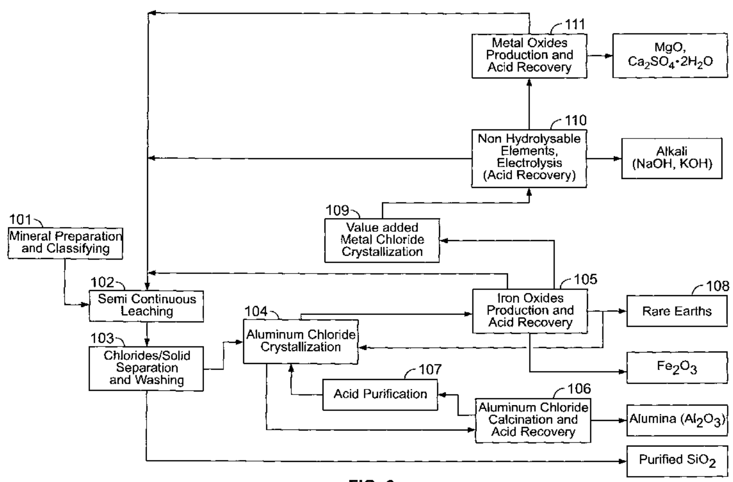


FIG. 6

**(57) Abstract**: There are provided processes for preparing alumina. These processes can comprise leaching an aluminum-containing material with HCl so as to obtain a leachate comprising aluminum ions and a solid, and separating said solid from said leachate; reacting said leachate with HCl so as to obtain a liquid and a precipitate comprising said aluminum ions in the form of $AlCl_3$, and separating said precipitate from said liquid; and heating said precipitate under conditions effective for converting $AlCl_3$ into $Al_2O_3$ and optionally recovering gaseous HCl so-produced. These processes can also be used for preparing various other products such as hematite, MgO, silica and oxides of various metals, sulphates and chlorides of various metals, as well as rare earth elements, rare metals and aluminum.

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# PROCESSES FOR PREPARING ALUMINA AND VARIOUS OTHER PRODUCTS

## CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] The present application claims priority on US 61/535,435 filed on September 16, 2011, on US 61/584,937 filed on January 10, 2012, and on US 61/668,646 filed on July 6, 2012. These documents are hereby incorporated by reference in their entirety.

## TECHNICAL FIELD

[0002] The present disclosure relates to improvements in the field of chemistry applied to the production of alumina. For example, it relates to processes for the production of alumina via the extraction of aluminum from aluminum-containing materials. These processes can also be efficient for preparing other products such as hematite, MgO, silica and oxides of various metals, sulphates and chlorides of various metals, as well as rare earth elements, rare metals and aluminum.

## BACKGROUND OF THE DISCLOSURE

[0003] There have been several known processes for the production of alumina. Many of them were using bauxite as starting material. These processes, that were mainly alkaline processes, have been employed throughout the years. Several of such alkaline processes have the disadvantage of being inefficient to segregate and extract value added secondary products, thus leaving an important environmental impact. There have also been development work employing hydrochloric acid for the leaching step but, it has been found that such processes were not efficient for removing most part of the impurities and especially iron. For example, removal of iron was also difficult to be carried out via adequate and economical techniques especially when using continuous processes.

## SUMMARY OF THE DISCLOSURE

**[0004]** According to one aspect, there is provided a process for preparing alumina and optionally other products, the process comprising :

leaching an aluminum-containing material with HCl so as to obtain a leachate comprising aluminum ions and a solid, and separating the solid from the leachate;

reacting the leachate with HCl so as to obtain a liquid and a precipitate comprising the aluminum ions in the form of $AlCl_3$, and separating the precipitate from the liquid;

heating the precipitate under conditions effective for converting $AlCl_3$ into $Al_2O_3$ and recovering gaseous HCl so-produced; and

recycling the gaseous HCl so-produced by contacting it with water so as to obtain a composition having a concentration higher than HCl azeotrope concentration ( 20.2 weight %) and reacting the composition with a further quantity of aluminum-containing material so as to leaching it.

**[0005]** According to another aspect, there is provided a process for preparing alumina and optionally other products, the process comprising :

leaching an aluminum-containing material with HCl so as to obtain a leachate comprising aluminum ions and a solid, and separating the solid from the leachate;

reacting the leachate with HCl so as to obtain a liquid and a precipitate comprising the aluminum ions in the form of $AlCl_3$, and separating the precipitate from the liquid;

heating the precipitate under conditions effective for converting $AlCl_3$ into $Al_2O_3$ and recovering gaseous HCl so-produced; and recycling the gaseous HCl so-produced by contacting it with water so as to obtain a composition having a concentration of about 18 to about 45 weight % or about 25 to about 45 weight % and reacting the composition with a further quantity of aluminum-containing material so as to leaching it.

**[0006]** According to another aspect, there is provided a process for preparing alumina and optionally other products, the process comprising :

leaching an aluminum-containing material with HCl so as to obtain a leachate comprising aluminum ions and a solid, and separating the solid from the leachate;

reacting the leachate with HCl so as to obtain a liquid and a precipitate comprising the aluminum ions in the form of $AlCl_3$, and separating the precipitate from the liquid;

heating the precipitate under conditions effective for converting $AlCl_3$ into $Al_2O_3$ and recovering gaseous HCl so-produced; and

recycling the gaseous HCl so-produced by contacting it with water so as to obtain a composition having a concentration of about 18 to about 45 weight % or about 25 to about 45 weight % and using the composition for leaching the aluminum-containing material.

**[0007]** According to another aspect, there is provided a process for preparing alumina and optionally other products, the process comprising :

leaching an aluminum-containing material with HCl so as to obtain a leachate comprising aluminum ions and a solid, and separating the solid from the leachate;

reacting the leachate with HCl so as to obtain a liquid and a precipitate comprising the aluminum ions in the form of $AlCl_3$, and separating the precipitate from the liquid;

heating the precipitate under conditions effective for converting $AlCl_3$ into $Al_2O_3$ and recovering gaseous HCl so-produced; and

recycling the gaseous HCl so-produced by contacting it with the leachate so as to precipitate the aluminum ions in the form of $AlCl_3{\bullet}6H_2O$.

**[0008]** According to another aspect, there is provided a process for preparing alumina and optionally other products, the process comprising :

leaching an aluminum-containing material with HCl so as to obtain a leachate comprising aluminum ions and a solid, and separating the solid from the leachate;

reacting the leachate with HCl so as to obtain a liquid and a precipitate comprising the aluminum ions in the form of $AlCl_3$, and separating the precipitate from the liquid; and

heating the precipitate under conditions effective for converting $AlCl_3$ into $Al_2O_3$.

**[0009]** According to another aspect, there is provided a process for preparing alumina and optionally other products, the process comprising :

leaching an aluminum-containing material with HCl so as to obtain a leachate comprising aluminum ions and a solid, and separating the solid from the leachate;

reacting the leachate with HCl so as to obtain a liquid and a precipitate comprising the aluminum ions in the form of $AlCl_3$, and separating the precipitate from the liquid; and

heating the precipitate under conditions effective for converting $AlCl_3$ into $Al_2O_3$ and optionally recovering gaseous HCl so-produced.

[0010] According to one aspect, there is provided a process for preparing aluminum and optionally other products, the process comprising :

leaching an aluminum-containing material with HCl so as to obtain a leachate comprising aluminum ions and a solid, and separating the solid from the leachate;

reacting the leachate with HCl so as to obtain a liquid and a precipitate comprising the aluminum ions in the form of $AlCl_3$, and separating the precipitate from the liquid;

heating the precipitate under conditions effective for converting $AlCl_3$ into $Al_2O_3$; and

converting $Al_2O_3$ into aluminum.

[0011] According to another aspect, there is provided a process for preparing aluminum and optionally other products, the process comprising :

leaching an aluminum-containing material with HCl so as to obtain a leachate comprising aluminum ions and a solid, and separating the solid from the leachate;

reacting the leachate with HCl so as to obtain a liquid and a precipitate comprising the aluminum ions in the form of $AlCl_3$, and separating the precipitate from the liquid;

heating the precipitate under conditions effective for converting $AlCl_3$ into $Al_2O_3$ and optionally recovering gaseous HCl so-produced; and

converting $Al_2O_3$ into aluminum.

## BRIEF DESCRIPTION OF DRAWINGS

**[0012]** In the following drawings, which represent by way of example only, various embodiments of the disclosure :

**[0013]** Fig. 1 shows a bloc diagram of an example of process for preparing alumina and various other products according to the present disclosure;

**[0014]** Fig. 2 is an extraction curve for Al and Fe in which the extraction percentage is expressed as a function of a leaching time in a process according to an example of the present application;

**[0015]** Fig. 3 shows a bloc diagram of another example of process for preparing alumina and various other products according to the present disclosure;

**[0016]** Fig. 4 is a schematic representation of an example of a process for purifying/concentrating HCl according to the present disclosure;

**[0017]** Fig. 5 is a schematic representation of an example of a process for purifying/concentrating HCl according to the present disclosure;

**[0018]** Fig. 6 shows another bloc diagram of an example of process for preparing alumina and various other products according to the present disclosure; and

**[0019]** Fig. 7 shows another bloc diagram of an example of process for preparing alumina and various other products according to the present disclosure.

## DETAILLED DESCRIPTION OF VARIOUS EMBODIMENTS

**[0020]** The following non-limiting examples further illustrate the technology described in the present disclosure.

**[0021]** The aluminum-containing material can be for example chosen from aluminum-containing ores (such as aluminosillicate minerals, clays, argillite, nepheline, mudstone, beryl, cryolite, garnet, spinel, bauxite, kaolin or mixtures thereof can be used). The aluminum-containing material can also be a recycled industrial aluminum-containing material such as slag, red mud or fly ashes.

**[0022]** The expression “red mud” as used herein refers, for example, to an industrial waste product generated during the production of alumina. For example, such a waste product can comprise silica, aluminum, iron, calcium, and optionally titanium. It can also comprise an array of minor constituents such as Na, K, Cr, V, Ni, Ba, Cu, Mn, Pb, and/or Zn etc. For example, red mud can comprises about 15 to about 80 % by weight of $Fe_2O_3$, about 1 to about 35 % by weight $Al_2O_3$, about 1 to about 65 % by weight of $SiO_2$, about 1 to about 20 % by weight of $Na_2O$, about 1 to about 20 % by weight of CaO, and from 0 to about 35 % by weight of $TiO_2$. According to another example, red mud can comprise about 30 to about 65 % by weight of $Fe_2O_3$, about 10 to about 20 % by weight $Al_2O_3$, about 3 to about 50 % by weight of $SiO_2$, about 2 to about 10 % by weight of $Na_2O$, about 2 to about 8 % by weight of CaO, and from 0 to about 25 % by weight of $TiO_2$.

**[0023]** The expression “fly ashes” as used herein refers, for example, to an industrial waste product generated in combustion. For example, such a waste product can contain various elements such as silica, oxygen, aluminum, iron, calcium. For example, fly ashes can comprise silicon dioxide ($SiO_2$) and aluminium oxide ($Al_2O_3$). For example, fly ashes can further comprises calcium oxide (CaO) and/or iron oxide ($Fe_2O_3$). For example fly ashes can comprise fine particles that rise with flue gases. For example, fly ashes can be produced during combustion of coal. For example, fly ashes can also comprise at least one element chosen from arsenic, beryllium, boron, cadmium, chromium, chromium VI, cobalt, lead, manganese, mercury, molybdenum, selenium, strontium, thallium, and/or vanadium. For example, fly ashes can also comprise rare earth elements and rare metals. For example, fly ashes can be considered as an aluminum-containing material.

[0024] The expression "slag" as used herein refers, for example, to an industrial waste product comprising aluminum oxide and optionally other oxides such as oxides of calcium, magnesium, iron, and/or silicon.

[0025] The expression "rare earth element" (also described as "REE") as used herein refers, for example, to a rare element chosen from scandium, yttrium, lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium. The expression "rare metals" as used herein refers, for example, to rare metals chosen from indium, zirconium, lithium, and gallium. These rare earth elements and rare metals can be in various form such as the elemental form (or metallic form), under the form of chlorides, oxides, hydroxides etc. The expression "rare earths" as used in the present disclosure as a synomym of "rare earth elements" that is described above.

[0026] The expression "at least one iron chloride" as used herein refers to $FeCl_2$, $FeCl_3$ or a mixture thereof.

[0027] The term "hematite" as used herein refers, for example, to a compound comprising $\alpha$-$Fe_2O_3$, $\gamma$-$Fe_2O_3$, $\beta$-FeO.OH or mixtures thereof.

[0028] The expression "iron ions" as used herein refers, for example to ions comprising to at least one type of iron ion chosen from all possible forms of Fe ions. For example, the at least one type of iron ion can be $Fe^{2+}$, $Fe^{3+}$, or a mixture thereof.

[0029] The expression "aluminum ions" as used herein refers, for example to ions comprising to at least one type of aluminum ion chosen from all possible forms of Al ions. For example, the at least one type of aluminum ion can be $Al^{3+}$.

[0030] The expression "at least one aluminum ion", as used herein refers, for example, to at least one type of aluminum ion chosen from all possible forms of Al ions. For example, the at least one aluminum ion can be $Al^{3+}$.

[0031] The expression "at least one iron ion", as used herein refers, for example, to at least one type of iron ion chosen from all possible forms of Fe ions. For example, the at least one iron ion can be $Fe^{2+}$, $Fe^{3+}$, or a mixture thereof.

**[0032]** The expression “at least one precipitated iron ion”, as used herein refers, for example, to at least one type of iron ion chosen from all possible forms of Fe ions that was precipitated in a solid form. For example, the at least one iron ion present in such a precipitate can be $Fe^{2+}$, $Fe^{3+}$, or a mixture thereof.

**[0033]** Terms of degree such as “about” and “approximately” as used herein mean a reasonable amount of deviation of the modified term such that the end result is not significantly changed. These terms of degree should be construed as including a deviation of at least ±5% or at least ±10% of the modified term if this deviation would not negate the meaning of the word it modifies.

**[0034]** For example, the aluminum-containing material can be leached with HCl having a concentration of about 10 to about 50 weight %, about 15 to about 45 weight %, of about 18 to about 45 weight % of about 18 to about 32 weight %, of about 20 to about 45 weight %, of about 25 to about 45 weight %, of about 26 to about 42 weight %, of about 28 to about 40 weight %, of about 30 to about 38 weight %, or between 25 and 36 weight %.

**[0035]** For example, the aluminum-containing material can be leached at a temperature of about 125 to about 225 °C, about 150 to about 200 °C, about 160 to about 190 °C, about 185 to about 190 °C, about 160 to about 180 °C, about 160 to about 175 °C, or about 165 to about 170 °C.

**[0036]** For example, the aluminum-containing material can be leached at a pressure of about 4 to about 10 barg, about 4 to about 8 barg, or about 5 to about 6 barg.

**[0037]** For example, the processes can further comprise recycling the gaseous HCl so-produced by contacting it with water so as to obtain a composition having a concentration of about 18 to about 45 weight % or 25 to about 45 weight %.

[0038] For example, the processes can further comprise recycling the gaseous HCl so-produced by contacting it with water so as to obtain a composition having a concentration of about 18 to about 45 weight % or about 25 to about 45 weight % and using the composition for leaching the aluminum-containing material.

[0039] For example, the liquid can comprise iron chloride. Iron chloride can comprise at least one of $FeCl_2$, $FeCl_3$, and a mixture thereof.

[0040] For example, the liquid can have an iron chloride concentration of at least 30% by weight; and can then be hydrolyzed at a temperature of about 155 to about 350 °C.

[0041] For example, the liquid can be concentrated to a concentrated liquid having an iron chloride concentration of at least 30% by weight; and then the iron chloride can be hydrolyzed at a temperature of about 155 to about 350 °C while maintaining a ferric chloride concentration at a level of at least 65% by weight, to generate a composition comprising a liquid and precipitated hematite, and recovering the hematite.

[0042] For example, non-hydrolysable elements with hematite can be concentrated back to a concentration of about 0.125 to about 52 % wt. in circulation loop in view of selective extraction.

[0043] For example, the liquid can be concentrated to a concentrated liquid having a concentration of the at least one iron chloride of at least 30% by weight; and then hydrolyzed at a temperature of about 155 to about 350 °C.

[0044] For example, the liquid can be concentrated to a concentrated liquid having a concentration of the at least one iron chloride of at least 30% by weight; and then the at least one iron chloride is hydrolyzed at a temperature of about 155 to about 350 °C while maintaining a ferric chloride concentration at a level of at least 65% by weight, to generate a composition comprising a liquid and precipitated hematite, and recovering the hematite.

[0045] For example, the liquid can be concentrated to a concentrated liquid having a concentration of the at least one iron chloride of at least 30% by weight; and then the at least one iron chloride is hydrolyzed at a temperature of about 155 to about 350 °C while maintaining a ferric chloride concentration at a level of at least 65% by weight, to generate a composition comprising a liquid and precipitated hematite; recovering the hematite; and recovering rare earth elements and/or rare metals from the liquid.

**[0046]** For example, the at least one iron chloride can be hydrolyzed at a temperature of about, 150 to about 175, 155 to about 170 or 165 to about 170 °C.

**[0047]** For example, the liquid can be concentrated to a concentrated liquid having an iron chloride concentration of at least 30% by weight; and then the iron chloride can be hydrolyzed at a temperature of about 155 to about 350 °C while maintaining a ferric chloride concentration at a level of at least 65% by weight, to generate a composition comprising a liquid and precipitated hematite; recovering the hematite; and recovering rare earth elements and/or rare metals from the liquid.

**[0048]** For example, the processes can further comprise, after recovery of the rare earth elements and/or rare metals, reacting the liquid with HCl so as to cause precipitation of $MgCl_2$, and recovering same.

**[0049]** For example, the processes can further comprise calcining $MgCl_2$ into MgO.

**[0050]** For example, the processes can further comprises, after recovery of the rare earth elements and/or rare metals, reacting the liquid with HCl, and substantially selectively precipitating $Na_2SO_4$. For example, $Na_2SO_4$ can be precipitated by reacting the liquid with $H_2SO_4$.

**[0051]** For example, the processes can further comprises, after recovery of the rare earth elements and/or rare metals, reacting the liquid with HCl, and substantially selectively precipitating $K_2SO_4$. For example,$K_2SO_4$ can be precipitated by adding $H_2SO_4$.

**[0052]** For example, the liquid can be concentrated to a concentrated liquid having an iron chloride concentration of at least 30% by weight; and then the iron chloride can be hydrolyzed at a temperature of about 155 to about 350 °C while maintaining a ferric chloride concentration at a level of at least 65% by weight, to generate a composition comprising a liquid and precipitated hematite; recovering the hematite; and reacting the liquid with HCl.For example, such processes can further comprises reacting the liquid with $H_2SO_4$ so as to substantially selectively precipitate $Na_2SO_4$. The processes can also comprise further reacting the liquid with $H_2SO_4$ so as to substantially selectively precipitating $K_2SO_4$.

**[0053]** For example, the processes can comprise reacting dry individual salts (for example Na or K salts) obtained during the processes with $H_2SO_4$ and recovering HCl while producing marketable $K_2SO_4$ and $Na_2SO_4$ and recovering hydrochloric acid of about 15 to about 90 % wt.

**[0054]** For example, sodium chloride produced in the processes can undergo a chemical reaction with sulfuric acid so as to obtain sodium sulfate and regenerate hydrochloric acid. Potassium chloride can undergo a chemical reaction with sulfuric acid so as to obtain potassium sulfate and regenerate hydrochloric acid. Sodium and potassium chloride brine solution can alternatively be the feed material to adapted small chlor-alkali electrolysis cells. In this latter case, common bases (NaOH and KOH) and bleach (NaOCl and KOCl) are produced.

**[0055]** For example, the processes can further comprise, after recovery of the rare earth elements and/or rare metals, recovering NaCl from the liquid, reacting the NaCl with $H_2SO_4$, and substantially selectively precipitating $Na_2SO_4$.

**[0056]** For example, the processes can further comprise, downstream of recovery of the rare earth elements and/or rare metals, recovering KCl from the liquid, reacting the KCl with $H_2SO_4$, and substantially selectively precipitating $K_2SO_4$.

**[0057]** For example, the processes can further comprise, downstream of recovery of the rare earth elements and/or rare metals, recovering NaCl from the liquid, carrying out an electrolysis to generate NaOH and NaOCl.

**[0058]** For example, the processes can further comprise, downstream of recovery of the rare earth elements and/or rare metals, recovering KCl from the liquid, reacting the KCl, carrying out an electrolysis to generate KOH and KOCl.

**[0059]** For example, the liquid can be concentrated to a concentrated liquid having a concentration of the at least one iron chloride of at least 30% by weight; and then the at least one iron chloride is hydrolyzed at a temperature of about 155 to about 350 °C while maintaining a ferric chloride concentration at a level of at least 65% by weight, to generate a composition comprising a liquid and precipitated hematite; recovering the hematite; and extracting NaCl and/or KCl from the liquid.

**[0060]** For example, the processes can further comprise reacting the NaCl with $H_2SO_4$ so as to substantially selectively precipitate $Na_2SO_4$.

**[0061]** For example, the processes can further comprise reacting the KCl with $H_2SO_4$ so as to substantially selectively precipitate $K_2SO_4$.

**[0062]** For example, the processes can further comprise carrying out an electrolysis of the NaCl to generate NaOH and NaOCl.

**[0063]** For example, the processes can further comprise carrying out an electrolysis of the KCl to generate KOH and KOCl.

**[0064]** For example, the processes can comprise separating the solid from the leachate and washing the solid so as to obtain silica having a purity of at least 95 %, at least 96%, at least 97%, at least 98%, at least 99%, at least 99.5 % or at least 99.9%.

**[0065]** For example, the processes can comprise reacting the leachate with gaseous HCl so as to obtain the liquid and the precipitate comprising the aluminum ions in the form of $AlCl_3 \cdot 6H_2O$.

**[0066]** For example, the processes can comprise reacting the leachate with dry gaseous HCl so as to obtain the liquid and the precipitate comprising the aluminum ions in the form of $AlCl_3 \cdot 6H_2O$.

**[0067]** For example, the processes can comprise reacting the leachate with acid of at least 30% wt. that was recovered, regenerated and/or purified as indicated in the present disclosure so as to obtain the liquid and the precipitate comprising the aluminum ions in the form of $AlCl_3•6H_2O$.

**[0068]**

**[0069]** For example, the processes can comprise reacting the leachate with gaseous HCl so as to obtain the liquid and the precipitate comprising said aluminum ions, the precipitate being formed by crystallization of $AlCl_3•6H_2O$.

**[0070]** For example, the processes can comprise reacting the leachate with dry gaseous HCl so as to obtain the liquid and the precipitate comprising the aluminum ions, the precipitate being formed by crystallization of $AlCl_3•6H_2O$.

**[0071]** For example, the gaseous HCl can have a HCl concentration of at least 85 % wt. or at least 90 % wt.

**[0072]** For example, the gaseous HCl can have a HCl concentration of about 90 % wt. or about 90 % to about 95 % wt..

**[0073]** For example, during the crystallization of $AlCl_3•6H_2O$, the liquid can be maintained at a concentration of HCl of about 25 to about 35 % by weight or about 30 to about 32 % by weight.

**[0074]** For example, the crystallization can be carried out at a temperature of about 45 to about 65 °C or about 50 to about 60 °C.

**[0075]** For example, the HCl can be obtained from the gaseous HCl so-produced.

**[0076]** For example, in the processes of the present disclosure, a given batch or quantity of the aluminum-containing material will be leached, will then be converted into $AlCl_3$ and when the HCl generated during calcination of $AlCl_3$ into $Al_2O_3$ will be used for example to leach another given batch or quantity of the aluminum-containing material.

[0077] For example, the processes can comprise heating the precipitate at a temperature of at least 850, 900, 925, 930, 1000, 1100, 1200 or 1250 °C for converting $AlCl_3$ into $Al_2O_3$.

[0078] For example, converting $AlCl_3$ into $Al_2O_3$ can comprise calcination of $AlCl_3$.

[0079] For example, calcination is effective for converting $AlCl_3$ into beta-$Al_2O_3$.

[0080] For example, calcination is effective for converting $AlCl_3$ into alpha-$Al_2O_3$.

[0081] For example, converting $AlCl_3$ into $Al_2O_3$ can comprise carrying out a calcination via a two-stage circulating fluid bed reactor.

[0082] For example, converting $AlCl_3$ into $Al_2O_3$ can comprise carrying out a calcination via a two-stage circulating fluid bed reactor that comprises a preheating system.

[0083] For example, converting $AlCl_3$ into $Al_2O_3$ can comprise carrying out a calcination at low temperature, for example, about 300 to about 600 °C, about 325 to about 550 °C, about 350 to about 500 °C, about 375 to about 450 °C, about 375 to about 425 °C, or about 385 to about 400 °C and/or injecting steam.

[0084] For example, converting $AlCl_3$ into $Al_2O_3$ can comprise carrying out a calcination at low temperature, for example, at least 350 °C and/or injecting steam.

[0085] For example, converting $AlCl_3$ into $Al_2O_3$ can comprise carrying out a calcination at low temperature, for example, less than 600 °C and/or injecting steam.

[0086] For example, converting $AlCl_3$ into $Al_2O_3$ can comprise carrying out a calcination by using coal as combustion source and by using a degasification unit.

[0087] For example, steam (or water vapor) can be injected at a pressure of about 200 to about 700 psig, about 300 to about 700 psig, about 400 to about 700 psig, about 550 to about 650 psig, about 575 to about 625 psig, or about 590 to about 610 psig.

[0088] For example, steam (or water vapor) can be injected and a plasma torch can be used for carrying fluidization.

[0089] For example, the steam (or water vapor) can be overheated.

[0090] For example, converting $AlCl_3$ into $Al_2O_3$ can comprise carrying out a calcination by means of carbon monoxide (CO).

[0091] For example, converting $AlCl_3$ into $Al_2O_3$ can comprise carrying out a calcination by means of a Refinery Fuel Gas (RFG).

[0092] For example, calcination can be carried out by injecting water vapor or steam and/or by using a combustion source chosen from fossil fuels, carbon monoxide, a Refinery Fuel Gas, coal, or chlorinated gases and/or solvants.

[0093] For example, calcination can be carried out by injecting water vapor or steam and/or by using a combustion source chosen from natural gas or propane.

[0094] For example, calcination can be carried out by providing heat by means of electric heating, gas heating, microwave heating,

[0095] For example, the fluid bed reactor can comprise a metal catalyst chosen from metal chlorides.

[0096] For example, thee fluid bed reactor can comprise a metal catalyst that is $FeCl_3$, $FeCl_2$ or a mixture thereof.

[0097] For example, the fluid bed reactor can comprise a metal catalyst that is $FeCl_3$.

[0098] For example, the preheating system can comprise a plasma torch.

[0099] For example, steam can be used as the fluidization medium heating. Heating can also be electrical.

**[00100]** For example, a plasma torch can be used for preheating the calcination reactor.

**[00101]** For example, a plasma torch can be used for preheating air entering in the calcination reactor.

**[00102]** For example, a plasma torch can be used for preheating a fluid bed.

**[00103]** For example, the calcination medium can be substantially neutral in terms of O2 (or oxidation). For example, the calcination medium can favorize reduction (for example a concentration of CO of about 100 ppm).

**[00104]** For example, the calcination medium is effective for preventing formation of $Cl_2$.

**[00105]** For example, the processes can comprise converting $AlCl_3{\bullet}6H_2O$ into $Al_2O_3$ by carrying out a calcination of $AlCl_3{\bullet}6H_2O$ that is provided by the combustion of gas mixture that comprises :

$CH_4$ : 0 to about 1% vol;

$C_2H_6$ : 0 to about 2% vol;

$C_3H_8$ : 0 to about 2% vol;

$C_4H_{10}$ : 0 to about 1% vol;

$N_2$ : 0 to about 0.5% vol;

$H_2$ : about 0.25 to about 15.1 % vol;

CO : about 70 to about 82.5 % vol; and

$CO_2$ : about 1.0 to about 3.5% vol.

**[00106]** Such a mixture can be efficient for reduction in off gas volume of 15.3 to 16.3%; therefore the capacity increases of 15.3 to 16.3 % proven on practical operation of the circulating fluid bed. Thus for a same flow it represents an Opex of 0.65*16.3% = 10.6%.

[00107] For example, the air to natural gas ratio of ($Nm^3/h$ over $Nm^3/h$) in the fluid bed can be about 9.5 to about 10

[00108] For example, the air to CO gas ratio of ($Nm^3/h$ over $Nm^3/h$) in the fluid bed can be about 2 to about 3.

[00109] For example, the processes can comprise, before leaching said aluminum-containing material, a pre-leaching removal of fluorine optionally contained in said aluminum-containing material.

[00110] For example, the processes can comprise leaching of the aluminum-containing material with HCl so as to obtain said leachate comprising aluminum ions and said solid, separating said solid from said leachate; and further treating said solid so as to separate $SiO_2$ from $TiO_2$ that are contained therein.

[00111] For example, the processes can comprise leaching said aluminum-containing material with HCl so as to obtain said leachate comprising aluminum ions and said solid, separating said solid from said leachate; and further treating said solid with HCl so as to separate $SiO_2$ from $TiO_2$ that are contained therein.

[00112] For example, the processes can comprise leaching said aluminum-containing material with HCl so as to obtain said leachate comprising aluminum ions and said solid, separating said solid from said leachate; and further treating said solid with HCl at a concentration of less than 20 % wt., at a temperature of less than 85 °C, in the presence of MgCl, so as to separate $SiO_2$ from $TiO_2$ that are contained therein.

[00113] For example, converting $AlCl_3$ into $Al_2O_3$ can comprise carrying out a one-step calcination.

[00114] For example, calcination can be carried out at different temperatures with steam. Temperature applied of superheated steam can be of about 350°C to about 550°C or about 350°C to about 940°C or about 350°C to about 1200°C.

[00115] For example, multi stage evaporation step of the hydrolyser can be carried out to reduce drastically energy consumption.

[00116] For example, the processes can be effective for providing an $Al_2O_3$ recovery yield of at least 93 %, at least 94 %, at least 95 %, about 90 to about 95 %, about 92 to about 95 %, or about 93 to about 95 %.

[00117] For example, the processes can be effective for providing a $Fe_2O_3$ recovery yield of at least 98 %, at least 99 %, about 98 to about 99.5 %, or about 98.5 to about 99.5 %.

[00118] For example, the processes can be effective for providing a MgO recovery yield of at least 96 %, at least 97 %, at least 98 %, or about 96 to about 98 %.

[00119] For example, the processes can be effective for providing a HCl recovery yield of at least 98 %, at least 99 %, or about 98 to about 99.9 %.

[00120] For example, the processes can be effective for providing chlorides of rare earth elements (REE-Cl) and chlorides of rare metals (RM-Cl) in recovery yields of about 75 % to about 96.5 % by using internal processes via an internal concentration loop.

[00121] For example, the processes can be effective for providing hydrochloric acid recovery yield of about 99.75 % with non-hydrolysable elements.

[00122] For example, the aluminum-containing material can be argillite.

[00123] For example, the aluminum-containing material can be bauxite.

[00124] For example, the aluminum-containing material can be red mud.

[00125] For example, the aluminum-containing material can be fly ashes.

[00126] For example, the aluminum-containing material can be chosen from industrial refractory materials.

[00127] For example, the aluminum-containing material chosen from aluminosilicate minerals.

[00128] For example, the processes can be effective for avoiding producing red mud.

[00129] For example, the alumina and the other products are substantially free of red mud.

[00130] For example, HCl can be recycled. For example, such a recycled HCl can be concentrated and/or purified.

[00131] For example, gaseous HCl can be concentrated and/or purified by means of $H_2SO_4$. For example, gaseous HCl can be passed through a packed column where it is contacted with a $H_2SO_4$ countercurrent flow. For example, by doing so, concentration of HCl can be increased by at least 50 % wt., at least 60 % wt., at least 70 % wt., at least 75 % wt., at least 80 % wt., about 50 % wt. to about 80 % wt., about 55 % wt. to about 75 % wt., or about 60 % wt. For example, the column can be packed with a polymer such as polypropylene(PP) or polytrimethylene terephthalate (PTT).

[00132] For example, gaseous HCl can be concentrated and/or purified by means of $CaCl_2$. For example, gaseous HCl can be passed through a column packed with $CaCl_2$.

[00133] For example, the processes can further comprise converting alumina ($Al_2O_3$) into aluminum. Conversion of alumina into aluminum can be carried out, for example, by using the Hall–Héroult process. References is made to such a well known process in various patents and patent applications such as US 20100065435; US 20020056650; US 5,876,584; US 6,565,733. Conversion can also be carried out by means of other methods such as those described in US 7,867,373; US 4,265,716; US 6,565,733 (converting alumina into aluminum sulfide followed by the conversion of aluminum sulfide into aluminum.). For example, aluminium can be produced by using a reduction environment and carbon at temperature below 200°C. Aluminum can also be produced by reduction using potassium and anhydrous aluminum chloride ( Wohler Process).

[00134] According to one example as shown in Fig. 1, the processes can involve the following steps (the reference numbers in Fig. 1 correspond to the following steps) :

1- The aluminum-containing material is reduced to an average particle size of about 50 to about 80 μm.

2- The reduced and classified material is treated with hydrochloric acid which allows for dissolving, under a predetermined temperature and pressure, the aluminum with other elements like iron, magnesium and other metals including rare earth elements and/or rare metals. The silica and titanium (if present in raw material) remain totally undissolved.

3- The mother liquor from the leaching step then undergoes a separation, a cleaning stage in order to separate the purified silica from the metal chloride in solution.

4- The spent acid (leachate) obtained from step 1 is then brought up in concentration with dry and highly concentrated gaseous hydrogen chloride by sparging this one into a crystallizer. This results into the crystallization of aluminum chloride hexahydrate (precipitate) with a minimum of other impurities. Depending on the concentration of iron chloride at this stage, further crystallization step(s) can be required. The precipitate is then separated from the liquid.

5- The aluminum chloride hexahydrate is then calcined (for example by means of a rotary kiln, fluid bed, etc) at high temperature in order to obtain the alumina form. Highly concentrated gaseous hydrogen chloride is then recovered and excess is brought in aqueous form to the highest concentration possible so as to be used (recycled) in the acid leaching step.

6- Iron chloride (the liquid obtained from step 4) is then pre-concentrated and hydrolyzed at low temperature in view of the $Fe_2O_3$ (hematite form) extraction and acid recovery from its hydrolysis. All heat recovery from the calcination step (step 5), the leaching part exothermic reaction (step 1) and other section of the processes is being recovered into the pre-concentrator.

10- After the removal of hematite, a solution rich in rare earth elements and/or rare metals can be processed. As it can be seen in Fig.3, an internal recirculation can be done (after the removal of hematite) and the solution rich in rare earth elements and/or rare metals can be used for crystallization stage 4. Extraction of the rare earth elements and/or rare metals can be done as described in PCT/CA2012/000253 and/or PCT/CA2012000419. These two documents are hereby integrated by reference in their entirety.

Other non-hydrolysable metal chlorides (Me-Cl) such as $MgCl_2$ and others then undergo the following steps:

7- The solution rich in magnesium chloride and other non-hydrolysable products at low temperature is then brought up in concentration with dry and highly concentrated gaseous hydrogen chloride by sparging it into a crystallizer. This results into the precipitation of magnesium chloride as an hexahydrate, for example after sodium and potassium chloride removal.

8- Magnesium chloride hexahydrate is then calcined (either through a rotary kiln, fluid bed, etc.) and hydrochloric acid at very high concentration is thus regenerated and brought back to the leaching step.

9- Other Me-Cl undergo a standard pyrohydrolysis step where mixed oxides (Me-O) can be produced and hydrochloric acid at the azeotropic point (20.2% wt.) is regenerated.

**[00135]** NaCl can undergo chemical reaction with $H_2SO_4$ to produce $Na_2SO_4$ and HCl at a concentration at or above azeotropic concentration. Moreover, KCl can undergo chemical reaction with $H_2SO_4$ to produce $K_2SO_4$ and HCl having a concentration that is above the azeotropic concentration. Sodium and potassium chloride brine solution can be the feed material to adapted small chlor-alkali electrolysis cells. In this latter case, common bases (NaOH and KOH) and bleach (NaOCl and KOCl) are produced as well as HCl.

**[00136]** For example, the liquid can be concentrated to a concentrated liquid having an iron chloride concentration of at least 30% by weight; and then the iron chloride can be hydrolyzed at a temperature of about 155 to about 350 °C while maintaining a ferric chloride concentration at a level of at least 65% by weight, to generate a composition comprising a liquid and precipitated hematite, and recovering the hematite.

**[00137]** For example, the liquid can be concentrated to a concentrated liquid having an iron chloride concentration of at least 30% by weight; and then the iron chloride can be hydrolyzed at a temperature of about 155 to about 350 °C while maintaining a ferric chloride concentration at a level of at least 65% by weight, to generate a composition comprising a liquid and precipitated hematite; recovering the hematite; and recovering rare earth elements and/or rare metals from the liquid. For example, the process can further comprise, after recovery of the rare earth elements and/or rare metals, reacting the liquid with HCl so as to cause precipitation of $MgCl_2$, and recovering same.

**[00138]** As previously indicated, various aluminum-containing materials can be used as starting material of the processes disclosed in the present disclosure. Examples with clays and bauxite have been carried out. However, the person skilled in the art will understand that the continuous processes can handle high percentages of silica (>55%) and impurities as well as relatively low percentages of aluminum (for example as low as about 15%) and still being economically and technically viable. Satisfactory yields can be obtained (>93-95%) on $Al_2O_3$ and greater than 75% on rare earth elements and/or rare metals. No pre-thermal treatment in most cases are required. The processes disclosed in the present disclosure involve special techniques on leaching and acid recovery at very high strength, thereby offering several advantages over alkaline processes.

[00139] In step 1 the mineral, whether or not thermally treated is crushed, milled, dried and classified to have an average particle size of about 50 to about 80 μm.

[00140] In step 2, the milled raw material is introduced into the reactor and will undergo the leaching phase.

[00141] The leaching hydrochloric acid used in step 2 can be a recycled or regenerated acid from steps 5, 6, 8, 9, 10 and 11 (see Fig. 3) its concentration can vary from 15% to 45% weight. percent. Higher concentration can be obtained using membrane separation, cryogenic and/or high pressure approach. The acid leaching can be carried out under pressure and at temperature close to its boiling point thus, allowing a minimal digestion time and extended reaction extent (90%-100%). Leaching (step 2) can be accomplished in a semi-continuous mode where spent acid with residual free hydrochloric acid is replaced by highly concentrated acid at a certain stage of the reaction or allowing a reduced acid/mineral ratio, thereby reducing reaction time and improving reaction kinetics. For example, kinetic constant k can be : 0.5 – 0.75 g/mole.L

[00142] As previously indicated, alkali metals, iron, magnesium, sodium, calcium, potassium, rare earth elements and other elements will also be in a chloride form at different stages. Silica will remain undissolved and will undergo (step 3) a liquid/solid separation and cleaning stage. The processes of the present disclosure tend to recover maximum amount of free hydrochloric acid left and chlorides in solution in order to maximize hydrochloric acid recovery yield, using techniques such as rake classifying, filtration with band filters, centrifugation, and others. Pure $SiO_2$ (one additional leaching stage) cleaning with nano water purity 99% min. Mother liquor free of silica is then named as spent acid (various metal chlorides and water) and goes to the crystallization step (step 4).

[00143] In step 4, the spent acid (or leachate) with a substantial amount of aluminum chloride is then saturated with dry and highly concentrated gaseous hydrogen chloride obtained or recycled from step 5 or with aqueous HCl >

30% wt., which results in the precipitate of aluminum chloride hexahydrate ($AlCl_3 \bullet 6H_2O$). The precipitate retained is then washed and filtered or centrifuged before being fed to the calcination stage (step 5). The remaining of the spent acid from step 4 is then processed to acid recovery system (steps 6 to 8) where pure secondary products will be obtained.

**[00144]** In step 5, aluminum oxide (alumina) is directly obtained from high temperature conditions. The highly concentrated hydrogen chloride in gaseous form obtained can be fed to steps 4 and 7 for crystallization where it can be treated through hydrophobic membranes. The excess hydrogen chloride is absorbed and used as regenerated acid to the leaching step 2 as highly concentrated acid, higher than the concentration at the azeotropic point (>20.2%). For example, such a concentration can be about 18 to about 45 weight %, about 25 to about 45 weight % or between 25 and 36 weight %.

**[00145]** After step 4, various chlorides derivatives (mainly iron with magnesium and rare earth elements and rare metals) are next subjected to an iron extraction step. Such a step can be carried out for example by using the technology disclosed in WO 2009/153321, which is hereby incorporated by reference in its entirety.

**[00146]** In step 6, a hydrolysis at low temperature (155-350°C) is carried out and pure $Fe_2O_3$ (hematite) is being produced and hydrochloric acid of at least 15% concentration is being regenerated. The method as described in WO 2009/153321 is processing the solution of ferrous chloride and ferric chloride, possible mixtures thereof, and free hydrochloric acid through a series of steps pre-concentration step, oxidation step where ferrous chloride is oxidized into ferric form, and finally through an hydrolysis step into an operational unit called hydrolyser where the ferric chloride concentration is maintained at 65 weight % to generate a rich gas stream where concentration ensures a hydrogen chloride concentration of 15-20.2% and a pure hematite that will undergo a physical separation step. Latent heat of condensation is recovered to the pre-concentration and used as the heating input with excess heat from the calcination stage (step 5).

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[00147] The mother liquor from the hydrolyser (step 6) can be recirculated partially to first step crystallization process where an increase in concentration of non-hydrolysable elements is observed. After iron removal, the liquor is rich in other non-hydrolysable elements and mainly comprises magnesium chloride or possible mixture of other elements (various chlorides) and rare earth elements and rare metals.

[00148] Rare earth elements and rare metals in form of chlorides are highly concentrated in percentage into the hydrolyser operational unit (step 6) and are extracted from the mother liquor (step 10) where various known techniques can be employed to extract a series of individual RE-O (rare earth oxides). Among others, the processes of the present disclosure allows to concentrate to high concentration the following elements, within the hydrolyser: scandium (Sc), galium (Ga), yttrium (Y), dysperosium (Dy), cerium (Ce), praseodynium (Pr), neodynium (Nd), europium (Eu), lanthanum (La), samarium (Sm), gadolinium, (Gd), erbium (Er), zirconium (Zr) and mixtures of thereof. Technologies that can be used for extracting rare earth elements and/or rare metals can be found, for example, in Zhou et al. in RARE METALS, Vol. 27, No. 3, 2008, p223-227, and in US 2004/0042945, hereby incorporated by reference in their entirety. The person skilled in the art will also understand that various other processes normally used for extracting rare earth elements and/or rare metals from the Bayer process can also be used. For example, various solvent extraction techniques can be used. For certain elements, a technique involving octylphenyl acid phosphate (OPAP) and toluene can be used. HCl can be used as a stripping agent. This can be effective for recovering $Ce_2O_3$, $Sc_2O_3$, $Er_2O_3$ etc. For example, different sequence using oxalic acid and metallic iron for ferric chloride separation can be used.

[00149] The spent acid liquor from steps 6 and 10 rich in value added metals, mainly magnesium, is processed to step 7. The solution is saturated with dry and highly concentrated gaseous hydrogen chloride from step 5, which results in the precipitation of magnesium chloride hexahydrate. For example, same can be accomplished with HCl in aqueous form over 30% wt.

The precipitate retained, is fed to a calcination stage step 8 where pure MgO (>98% wt.) is obtained and highly concentrated hydrochloric acid (for example of at least 38 %) is regenerated and diverted to the leaching step (step 2). An alternative route for step 7 is using dry gaseous hydrochloric acid from step 8.

[00150] In step 9, metal chlorides unconverted are processed to a pyrohydrolysis step (700-900°C) to generate mixed oxides and where hydrochloric acid from 15-20.2% wt. concentration can be recovered.

[00151] According to another example as shown in Fig. 3, the processes can be similar to the example shown in Fig, 1 but can comprise some variants as below discussed.

[00152] In fact, as shown in Fig. 3, the processes can comprise (after step 6 or just before step 10) an internal recirculation back to the crystallization step 4. In such a case, The mother liquor from the hydrolyser (step 6) can be recirculated fully or partially to the crystallization of step 4 where a concentration increase will occur with respect to the non-hydrolysable elements including rare earth elements and/or rare metals.

[00153] Such a step can be useful for significantly increasing the concentration of rare earth elements and/or rare metals, thereby facilitating their extraction in step 10.

[00154] With respect to step 7, the solution rich in magnesium chloride and other non-hydrolysable products at low temperature is, as previously discussed, then brought up in concentration with dry and highly concentrated gaseous hydrogen chloride by sparging it into a crystallizer. This can result into the precipitation of magnesium chloride as an hexahydrate (for example after sodium and potassium chloride removal). This can also be accomplished with HCl in aqueous form.

[00155] As shown in Fig. 3, an extra step 11 can be added. Sodium chloride can undergo a chemical reaction with sulfuric acid so as to obtain sodium sulfate and regenerate hydrochloric acid at a concentration at or above the azeotropic point. Potassium chloride can undergo a chemical reaction with sulfuric acid so as to obtain potassium sulfate and regenerate hydrochloric

acid at a concentration above the azeotropic concentration. Sodium and potassium chloride brine solution can be the feed material to adapted small chlor-alkali electrolysis cells. In this latter case, common bases (NaOH and KOH) and bleach (NaOCl and KOCl) are produced and can be reused to some extent in other areas of the processes of the present disclosure (scrubber, etc.).

**[00156]** The following are non-limitative examples.

**Example 1**

**Preparation of alumina and various other products**

**[00157]** As a starting material a sample of clay was obtained from the Grande Vallée area in Québec, Canada.

**[00158]** These results represent an average of 80 tests carried out from samples of about 900 kg each.

**[00159]** Crude clay in the freshly mined state after grinding and classification had the following composition:

$Al_2O_3$ : 15% - 26%;

$SiO_2$ : 45% - 50%;

$Fe_2O_3$ : 8% - 9%;

MgO : 1% – 2%;

Rare earth elements and/or rare metals : 0.04% - 0.07%;

LOI : 5% - 10%.

**[00160]** This material is thereafter leached in a two-stage procedure at 140-170 °C with 18-32 weight % HCl. The HCl solution was used in a stoichiometric excess of 10-20% based on the stoichiometric quantity required for the removal of the acid leachable constituents of the clay. In the first leaching stage of the semi-continuous operation (step 2), the clay was contacted for 2.5 hours with required amount or certain proportion of the total amount of hydrochloric acid. After removal of the spent acid, the clay was contacted again with a minimum 18 weight % hydrochloric acid solution for about 1.5 hour at same temperature and pressure.

**[00161]** A typical extraction curve obtained for both iron and aluminum for a single stage leaching is shown in Fig. 2.

**[00162]** The leachate was filtered and the solid was washed with water and analyzed using conventional analysis techniques (see step 3 of Fig. 1). Purity of obtained silica was of 95.4% and it was free of any chlorides and of HCl.

**[00163]** After the leaching and silica removal, the concentration of the various metal chlorides was :

$AlCl_3$ : 15-20%;

$FeCl_2$ : 4-6%;

$FeCl_3$ : 0.5-2.0%;

$MgCl_2$ : 0.5-2.0 %;

Free HCl : 5-50 g/l

**[00164]** Spent acid was then crystallized using about 90 to about 98% pure dry hydrochloric acid in gas phase in two stages with less than 25 ppm iron in the aluminum chloride hexahydrate formed. The concentration of HCl in solution (aqueous phase) was about 22 to about 32% or 25 to about 32 % The recovered crystallized material (hydrate form of $AlCl_3$ having a minimum purity of 99.8 %) was then calcined at 930°C or 1250°C, thus obtaining the α-portion of the alumina.

**[00165]** HCl concentration in gas phase exiting the calcination stage was having a concentration greater than 30% and was used (recycled) for crystallization of the $AlCl_3$ and $MgCl_2$. Excess of hydrochloric acid is absorbed at the required and targeted concentration for the leaching steps.

**[00166]** Iron chloride (about 90-95% in ferric form) is then sent to a hydrothermal process in view of its extraction as pure hematite ($Fe_2O_3$). This can be done by using the technology described in WO 2009/153321 of low temperature hydrolysis with full heat recovery from calcining, pyrohydrolysis and leaching stage.

**[00167]** Rare earth elements and rare metals are extracted from the mother liquor of the hydrolyzer where silica, aluminum, iron and a great portion of water have been removed and following preconcentration from hydrolyser to crystallization. It was observed that rare earth elements can be concentrated by a factor of about 4.0 to 10.0 on average within the hydrolyzer itself on a single pass through it i.e. without concentration loop. The following concentration factors have been noted within the hydrolyzer (single pass):

Ce > 6

La > 9

Nd > 7

Y > 9

**[00168]** Remaining magnesium chloride is sparged with dry and highly concentrated hydrochloric acid and then calcinated to MgO while recovering high concentration acid (for example up to 38.4%).

**[00169]** Mixed oxides (Me-O) containing other non-hydrolysable components were then undergoing a pyrohydrolysis reaction at 700-800$^{o}$C and recovered acid (15-20.2% wt.) was rerouted for example to the leaching system.

**Overall yields obtained:**

$Al_2O_3$ : 93-95% recovery;

$Fe_2O_3$ : 98-99.5% recovery;

Rare earth elements and/or rare metals : 75-93% minimum recovery;

MgO : 96-98% recovery;

Material discarded : 0-5% maximum;

HCl global recovery : 99.75% minimum;

HCl strength as feed to leaching 18-32%;

Red mud production : None.

**Example 2**

**Preparation of alumina and various other products**

**[00170]** A similar feed material (bauxite instead of clay) was processed as per in example 1 up to the leaching stage and revealed to be easily leachable under the conditions established in example 1. It provided an extraction percentage of 100% for the iron and over 90-95% for aluminum. The technology was found to be economically viable and no harmful by-products (red mud) were generated. Samples tested had various concentrations of $Al_2O_3$ (up to 51%), $Fe_2O_3$ (up to 27%) and MgO (up to 1.5%).

**Example 3**

**HCl gas enrichment and purification: $H_2SO_4$ route**

**[00171]** $H_2SO_4$ can be used for carrying out purification of HCl. It can be carried out by using a packing column with $H_2SO_4$ flowing counter currently (see Fig. 4). This allows for converting the recovered HCl into HCl having a concentration above the azeotropic point (20.1% wt) and increase its concentration by about 60 to about 70% at minimum.

**[00172]** Water is absorbed by $H_2SO_4$ and then $H_2SO_4$ regeneration is applied where $H_2SO_4$ is brought back to a concentration of about 95 to about 98% wt. Water release at this stage free of sulphur is recycled back and used for crystallization dissolution, etc. Packing of the column can comprise polypropylene or polytrimethylene terephthalate (PTT).

[00173] Combustion energy can be performed with off gas preheating air and oxygen enrichment. Oxygen enrichment: +2% represents flame temperature increase by: 400°C maximum.

**Example 4**

**HCl gas enrichment and purification: calcium chloride to calcium chloride hexahydrate (absorption / desorption process)**

[00174] As shown in Fig. 5, $CaCl_2$ can be used for drying HCl. In fact, $CaCl_2$ can be used for absorbing water contained into HCl. In such a case, $CaCl_2$ is converted into its hexachloride form ($CaCl_2 \bullet H_2O$) and one saturated system is eventually switched into regeneration mode where hot air recovered from calcination off gas of alumina and magnesium oxide spray roasting is introduced to regenerate the fixed bed. Such an ion / exchange type process can be seen in Fig. 4 and the cycle can be inversed to switch from one column to another one.

[00175] The person skilled in the art would understand that the processes described in examples 3 and 4 can be used in various different manners. For example, these processes can be combined with the various processes presented in the present disclosure. For example, such purifications techniques can be integrated to the processes shown in Figs. 1, 3 or 6. For example, these techniques can be used downstream of at least one of step chosen from steps 5, 6, 8, 9, 10 and 11 (see Figs. 1 and 3). They can also be used downstream of step 4 and/or step 7. They can also be used downstream of at least one of step chosen from steps 104 to 111 (see Fig. 6)

**Example 5**

**Preparation of alumina and various other products**

[00176] This example was carried out by using a process as represented in Figs. 6 and 7. It should be noted that the processes represented in Figs. 6 and 7 differ only by the fact that Fig. 7 show to additional stages i.e. stages 112 and 113.

**Raw material preparation**

**[00177]** Raw material, clay for example, was processed in a secondary crusher in the clay preparation plant 101. Dry milling and classifying occurs on a dry basis in vertical roller mills (for example Fuller-Loesche LM 30.41). The clay preparation 101 included three roller mills; two running at a capacity of approximately 160-180 tph and one on standby. Raw material, if required, can be reduced to 85% less than 63 microns. Processed material was then stored in homogenization silos before being fed to the acid leaching plant 102. Below in Table 1 are shown results obtained during stage 101. If the ore contains the fluorine element, a special treatment can be applied before carrying out the 102 stage. In presence of hydrochloric acid, fluorine can produce hydrofluoric acid. This acid is extremely corrosive and damaging for human health. Thus, before leaching 102, an optional treatment fluorine separation 112 can be done. Stage 112 can comprise treating the processed material coming from stage 101 with an acid in a pre-leaching treatment so as to remove hydrofluoric acid. Therefore, depending on the composition of the raw material, a fluorine separation stage 112 (or pre-leaching stage 112) can be carried out.

Table 1.

| Clay preparation | | |
|---|---|---|
| Rate | 290 tph | |
| Composition feed (main constituents) | $SiO_2$: | 50.9% |
| | $Al_2O_3$: | 24.0% |
| | $Fe_2O_3$: | 8.51% |
| | CaO: | 0.48% |
| | MgO: | 1.33% |
| | $Na_2O$: | 1.06% |
| | $K_2O$: | 2.86% |
| | MnO: | 0.16% |
| | $Cr_2O_3$: | 0.01% |
| | $TiO_2$: | 0.85% |
| | $P_2O_5$: | 0.145% |
| | SrO: | 0.015% |
| | BaO: | 0.05% |

| Clay preparation | | |
|---|---|---|
| | $V_2O_5$ | 0.0321% |
| | Other (including $H_2O$ and REE): | 9.63% |
| Obtained particle size | 85% < 63 μm | |
| Residual moisture | 0.5-0.7% | |
| Yield | 99.5% min | |

**Acid Leaching**

**[00178]** Next, acid leaching 102 was performed semi-continuously in an 80 m³ glass-lined reactor. Semi-continuous mode comprises replacing reacted acid 1/3 in the reaction period with higher concentration regenerated acid, which greatly improves reaction kinetics. The reactor arrangement comprises for example, a series of three reactors.

**[00179]** Leaching was performed at high temperature and pressure (about 160 to about 195°C and pressures of about 5 to about 8 barg) for a fixed period of time. Reaction time was a function of the reaction extent targeted (98% for $Al_2O_3$), leaching mode, acid strength, and temperature/pressure applied.

**[00180]** Spent acid recovered out of the acid leaching 102 was then filtered 103 from unreacted silica and titanium dioxide and washed through an automated filter press where all free HCl and chloride are recovered. This allows, for example, a maximum quantity of about 30 ppm $SiO_2$ going into spent liquor. Cleaned silica at a concentration of ≈96 % + $SiO_2$ is then produced. Various options are possible at that point. For example, the 96% silica can undergo final neutralization through caustic bath, cleaning, and then bricketing before storage. According to another example, the silica purified by adding another leaching step followed by a solid separation step that ensures $TiO_2$ removal (see stage 113 in Fig. 7). In that specific case, high purity silica 99.5%+ is produced. In stage 113, titanium and silicium can be separated from one another in various manners. For example, the solid obtained from stage 103 can be leached in the presence of $MgCl_2$ at a temperature below 90 or 80 °C and at low acid concentration. For example, acid concentration can be below 25 or 20 %. The acid can be HCl or $H_2SO_4$. In such a case, titanium remains soluble after such a leaching while titanium is still in a solid form. These solid and liquid obtained after stage 113 are thus separated to provide eventually $TiO_2$ and $SiO_2$. Water input and flow for silica cleaning is in a ratio of 1:1 (silica/water) (150 t/h $SiO_2$ / 150 t/h $H_2O$), but comprises of wash water circulation in closed loop in the process and limited amount of process water for final cleaning of the silica and recovery of all chlorides and free HCl generated at the leaching stage. Below in Table 2 are shown results obtained during stage 102.

Table 2.

| | | |
|---|---|---|
| Acid Leaching | | |
| Equivalent solid feed rate | 259.6 tph | |
| Operation mode | Semi-continuous | |
| Acid to clay ratio | 3.10 @ 23% wt (Equivalent to 3.35 with semi-continuous at 18.0 % wt) | |
| Regenerated acid concentration | 18.0-32.0% | |
| Operating temperature | 150-155°C (Pilot) 165-200°C ( Plant) | |
| MAWP | 120 psig | |
| Typical chemical reactions | $Fe_2O_3 + 6\ HCl \rightarrow 2\ FeCl_3 + 3H_2O$ | |
| | $Al_2O_3 + 6\ HCl \rightarrow 2\ AlCl_3 + 3\ H_2O$ | |
| | $MgO + 2\ HCl \rightarrow MgCl_2 + H_2O$ | |
| | $K_2O + 2\ HCl \rightarrow 2\ KCl + H_2O$ | |
| | $Re_2O_3 + 6\ HCl \rightarrow 2\ ReCl_3 + 3H_2O$ | |
| Spent acid flow to crystallization | 600-1100 $m^3/h$ | |
| Practical chemical composition after step 102 without solid ($SiO_2$) | $FeCl_3$ | 4.33% |
| | $FeCl_2$ | 0.19% |
| | $AlCl_3$ | 16.6% |
| | $MgCl_2$ | 0.82% |
| | NaCl | 1.1% |
| | KCl | 1.2% |
| | $CaCl_2$ | 0.26% |
| Extraction yields | Iron | 100% |
| | $Al_2O_3$ | 98% |
| $SiO_2$ Recovery | 99.997% | |

| Acid Leaching | |
|---|---|
| Energy consumption | Activation energy only and self-sustained exothermic reaction from 130°C<br>Heat is recovered and sent to 10% |

**$AlCl_3$ Crystallization**

**[00181]** Spent acid, with an aluminum chloride content of about 20 to about 30 %, was then processed in the crystallization stage 104. Dry and highly concentrated HCl (> 90% wt.) in gas phase was sparged in a two-stage crystallization reactor, which allows the crystallization of aluminum chloride hexahydrate.

**[00182]** The flow rate of acid through these reactors is about 600 to about 675 $m^3/h$ and the reactor was maintained at about 50 to about 60°C during this highly exothermic reaction. Heat was recovered and exchanged to the acid purification 107 part of the plant thus ensuring proper heat transfer and minimizing heat consumption of the plant. Aluminum chloride solubility decreases rapidly, compared to other elements, with the increase in concentration of free HCl in the crystallization reactor. The concentration of $AlCl_3$ for precipitation/crystallization was about 30%

**[00183]** The HCl concentration during crystallization was thus about 30 to about 32 % wt.

**[00184]** The aqueous solution from the crystallization stage 104 was then submitted to the hydrothermal acid recovery plant 105, while the crystals are processed through the decomposition/calcination stage in the calcination plant 106.

**[00185]** A one-step crystallization stage or a multi-step crystallization stage can be done. For example, a two-steps crystallization stage can be carried out.

**[00186]** Below in Tables 3A and 3B are shown results obtained during stage 104.

Table 3A.

| Aluminum chloride crystallization | |
|---|---|
| Number of crystallization steps | 2 |
| Operating temperature | 50-60°C |
| Sparging HCl concentration | 90% (gaseous) |
| Typical chemicals formed | $AlCl_3 \cdot 6H_2O$ (s)<br>Metal chlorides (aq) |
| $AlCl_3 \cdot 6H_2O$ residual | < 5% (practical); 8% |

Table 3B.

**Typical crystals composition main constituents obtained at pilot scale and feeding calcination**

| Component | Weight distribution (%) |
|---|---|
| $AlCl_3 \cdot 6H_2O$ | 99.978 |
| $BaCl_2 \cdot 2H_2O$ | 0.0000 |
| $CaCl_2 \cdot 6H_2O$ | 0.0009 |
| $CrCl_4$ | 0.0022 |
| $CuCl_2 \cdot 2H_2O$ | 0.0000 |
| $FeCl_3 \cdot 6H_2O$ | 0.0019 |
| KCl | 0.0063 |
| $MgCl_2 \cdot 6H_2O$ | 0.0093 |
| $MnCl_2 \cdot 4H_2O$ | 0.0011 |
| NaCl | 0.0021 |
| $SiCl_4$ | 0.0004 |
| $SrCl_2 \cdot 6H_2O$ | 0.0000 |
| $TiCl_4$ | 0.0001 |
| $VCl_4$ | 0.0000 |
| Free $Cl^-$ | 0.0000 |

**Calcination and hydrothermal acid recovery**

**[00187]** The calcination 106 comprises the use of a two-stage circulating fluid bed (CFB) with preheating systems. The preheating system can comprise a plasma torch to heat up steam to process. It processes crystals in the decomposition/calcination stage. The majority of the hydrochloric acid was released in the first stage which was operated at a temperature of about 350°C, while the second stage performs the calcination itself. Acid from both stages (about 66 to about 68% of the recovered acid from the processes) was then recovered and sent to either to the acid leaching 102 or to the acid purification 107. In the second reactor, which was operated at a temperature of about 930°C, acid was recovered through the condensation and absorption into two columns using mainly wash water from the acid leaching sector 102. Latent heat from this sector was recovered at the same time as large amounts of water, which limits net water input.

[00188] In the iron oxides productions and acid recovery 105 system, which comprises, aqueous solution from the crystallization 104 first undergoes a pre-concentration stage followed by processing in the hydrolyzer reactor. Here, hematite was produced during low temperature processing (about 165°C). A recirculation loop was then taken from the hydrolyzer and is recirculated to the pre-concentrator, allowing the concentration of REE, Mg, K, and other elements. This recirculation loop, allows rare earth element chlorides and/or rare metal chlorides and various metal chlorides concentration to increase without having these products precipitating with hematite up to a certain extent.

[00189] Depending on acid balance in the plant, recovered acid is sent either directly to the 102 or 107 stage.Table 4 shows results obtained in stage 105.

Table 4.

| Hydrothermal acid recovery | |
|---|---|
| Flowrate from crystallization to HARP | 592 $m^3/h$ (design)<br>600 $m^3/h$ (design) |
| Operating hydrolyser temperature | 155-170°C |
| Regenerated acid concentration | 27.4% |
| Regenerated acid flowrate | 205.2 tph HCl |
| Hematite total production rate | 24 TPH (design) |
| HCl recovery | > 99.8% |
| Reflux (recirculation loop) rate in between hydrolyzer and pre-concentrator | 56 tph |
| Rare earth element chlorides and/or rare metal chlorides rate in recirculation loop | ≈ 12.8 t/h |

| **Hematite quality obtained and/or projected** | |
|---|---|
| $Fe_2O_3$ purity | > 99.5% |
| Hydrolysable chlorides | < 0.2% |
| Moisture | Max 20% after filtration |
| PSD | 25-35 microns |
| Density (bulk) | 2-3 kg/l |

| **Typical chemical reaction in stage 105** |
|---|
| $2FeCl_3 + 3H_2O \rightarrow Fe_2O_3 + 6\ HCl$<br>155-170°C |

[00190] Table 5 shows results obtained in stage 106.

Table 5.

| Calcination Plant 106 | |
|---|---|
| Process characteristics: | • Two-stage circulating fluid bed (CFB) with pre-heating system<br>• Two-stage hydrochloric acid regeneration |
| Production rate (practical) | About 66 tph |
| CFB feed rate | 371 tph @ 8% humidity* |

*High side since crystals will be at ≈ 2-3% moisture.

| **Typical chemical reaction occurring** |
|---|
| $2(AlCl_3 \cdot 6\ H_2O) + Energy \rightarrow Al_2O_3 + 6\ HCl + 9H_2O$ |

| **Typical alumina chemical composition obtained from aluminum chloride hexahydrate crystals being fed to calcination** | |
|---|---|
| **Component** | **Weight distribution (%)** |
| $Al_2O_3$ | 99.938 |
| $Fe_2O_3$ | 0.0033 |
| $SiO_2$ | 0.0032 |
| $Cr_2O_3$ | 0.0063 |
| $V_2O_5$ | 0.0077 |
| Na | 0.0190 |
| MgO | 0.0090 |
| $P_2O_5$ | 0.0039 |

| | |
|---|---|
| K | 0.0053 |
| Ca | 0.0020 |
| MnO | 0.0002 |
| Free $Cl^-$ | Undetectable |

**Rare earth elements and rare metals extractions**

**[00191]** The stream that was taken out of 105 recirculation then was treated for rare earth elements and are metals extraction 108, in which the reduction of the remaining iron back to iron 2 ($Fe^{2+}$), followed by a series of solvent extraction stages, was performed. The reactants were oxalic acid, NaOH, DEHPA (Di-(2-ethylhexyl)phosphoric acid) and TBP (tri-n-butyl phosphate) organic solution, kerosene, and HCl were used to convert rare earth element chlorides and rare metals chlorides to hydroxides. Countercurrent organic solvent with stripping of solution using HCl before proceeding to specific calcination from the rare earth elements and rare metals in form of hydroxide and conversion to high purity individual oxides. A ion exchange technique is also capable of achieving same results as polytrimethylen terephtalate (PET) membrane.

**[00192]** Iron powder from 105, or scrap metal as FeO, can be used at a rate dependent on $Fe^{3+}$ concentration in the mother liquor. HCl (100% wt) at the rate of 1 tph can be required as the stripped solution in REE Solvent Extraction (SX) separation and re-leaching of rare earth elements and/or rare metals oxalates.

**[00193]** Water of very high quality, demineralized or nano, at the rate of 100 tph was added to the strip solution and washing of precipitates.

**[00194]** Oxalic acid as di-hydrate at a rate of 0.2 tph was added and contributes to the rare earth elements and rare metals oxalates precipitation. NaOH or MgOH at a rate of 0.5 tph can be used as a neutralization agent.

**[00195]** DEHPA SX organic solution at the rate of 500 g/h was used as active reagent in rare earth elements separation while TBP SX organic solution at the rate of 5 kg/h is used as the active reagent for gallium recovery and yttrium separation. Finally, a kerosene diluent was used at the rate of approximately 2 kg/h in all SX section. Calcination occurs in an electric rotary furnace via indirect heating to convert contents to $REE_2O_3$ (oxides form) and maintain product purity.

**[00196]** Results of various tests made regarding stage 108 are shown in Table 6.

One line divided in subsections (5) to isolate the following elements using solvent extraction:

- $Ga_2O_3$
- $Y_2O_3$
- $Sc_2O_3$
- $Eu_2O_3 + Er_2O_3 + Dy_2O_3$
- $Ce_2O_3 + Nd_2O_3 + Pr_2O_3$

| | | | |
|---|---|---|---|
| Equivalent output earths oxides | | | 166.14 kg/h |
| **Projected production as per pilot testing results** | | | |
| | | | |
| Feed | Incoming (kg/h) | | Final extraction individual (kg/h) |
| $Ga_2O_3$ | 15.66 | | 11.98 |
| $Sc_2O_3$ | 9.06 | | 8.11 |
| $Y_2O_3$ | 22.56 | | 20.22 |
| $La_2O_3$ | 32.24 | | 25.67 |
| $Ce_2O_3$ | 61.37 | | 51.82 |
| $Pr_2O_3$ | 8.08 | | 6.18 |
| $Nd_2O_3$ | 30.3 | | 27.24 |
| $Sm_2O_3$ | 5.7 | | 4.51 |
| $Eu_2O_3$ | 1.06 | | 0.95 |
| $Gd_2O_3$ | 4.5 | | 4.06 |
| $Dy_2O_3$ | 3.9 | | 3.55 |
| $Er_2O_3$ | 2.1 | | 1.86 |
| **Total** | **196.55** | | **166.14** |

**Global yield : 84.53%**

[00197] Alternatively, stage 108 can be carried out as described in PCT/CA2012/000253 and/or PCT/CA2012000419.

[00198] The solution after stages 108 and 109 contained mainly $MgCl_2$, NaCl, KCl, $CaCl_2$, $FeCl_2/FeCl_3$, and $AlCl_3$ (traces), and then undergoes the 111 stage.Na, K, Ca that follows the MgO can be extracted in stage 110 by crystallization in a specific order; Na first, followed by K, and then Ca. This technique can be employed for example in the Israeli Dead Sea salt processing plant to produce MgO and remove alkali from the raw material.

**HCl regeneration**

[00199] Alkali (Na, K), once crystallized, was sent and processed in the alkali hydrochloric acid regeneration plant 110 for recovering highly concentrated hydrochloric acid (HCl). The process chosen for the conversion can generate value-added products

[00200] Various options are available to convert NaCl and KCl with intent of recovering HCl. One example can be to contact them with highly concentrated sulfuric acid ($H_2SO_4$), which generates sodium sulphate ($Na_2SO_4$) and potassium sulfate ($K_2SO_4$), respectively, and regenerates HCl at a concentration above 90% wt. Another example, is the use of a sodium and potassium chloride brine solution as the feed material to adapted small chlor-alkali electrolysis cells. In this latter case, common bases (NaOH and KOH) and bleach (NaOCl and KOCl) are produced. The electrolysis of both NaCl and KCl brine is done in different cells where the current is adjusted to meet the required chemical reaction. In both cases, it is a two-step process in which the brine is submitted to high current and base (NaOH or KOH) is produced with chlorine ($Cl_2$) and hydrogen ($H_2$). $H_2$ and $Cl_2$ are then submitted to a common flame where highly concentrated acid in gas (100% wt.) phase is produced and can be used directly in the crystallization stage 104, or to crystallization stages requiring dry highly concentrated acid.

**Magnesium oxide**

[00201] The reduced flow, which was substantially free of most elements (for example $AlCl_3$, $FeCl_3$, REE-Cl, NaCl, KCl) and rich in $MgCl_2$, was then

submitted to the magnesium oxides plant 111. In the MgO, pyrohydrolysis of $MgCl_2$ and any other leftover impurities were converted into oxide while regenerating acid. The first step was a pre-evaporator/crystallizer stage in which calcium is removed and converted into gypsum ($CaSO_4 \cdot 2H_2O$) by a simple chemical reaction with sulfuric acid, for which separation of MgO is required. This increases the capacity of MgO roasting and also energy consumption slightly, while substantially recovering HCl. The next step was the specific pyrohydrolysis of MgO concentrated solution by spray roasting. Two (2) main products were generated; MgO that was further treated and HCl (about 18% wt.), which was either recycled back to the upstream leaching stage 102 or to the hydrochloric acid purification plant (107 The MgO-product derived from the spray roaster can require further washing, purification, and finally calcining depending on the quality targeted. The purification and calcining can comprise a washing-hydration step and standard calcining step.

**[00202]** The MgO from the spray roaster is highly chemically active and wasdirectly charged into a water tank where it reacts with water to form magnesium hydroxide, which has poor solubility in water. The remaining traces of chlorides, like $MgCl_2$, NaCl, dissolved in water. The $Mg(OH)_2$ suspension, after settling in a thickener, was forwarded to vacuum drum filters, which remove the remaining water. The cleaned $Mg(OH)_2$ is then forwarded into a calcination reactor where it is exposed to high temperatures in a vertical multi-stage furnace. Water from hydration is released and allows the transformation of the $Mg(OH)_2$ to MgO and water. At this point, the magnesium oxide was of high purity (> 99%).

**HCl purification**

**[00203]** The hydrochloric acid purification stage 107 is effective for purifying HCl regenerated from different sectors (for example 105, 106, 111) and to increase its purity for crystallization, whereas dry highly concentrated acid (> 90% wt.) can be used as the sparging agent. Stage 107 also allowed for controlling the concentration of the acid going back to stage 102 (about 22 to about 32% wt.) and allows total acid and water balance. Total plant water balance is performed mainly by reusing wash water as absorption medium, as quench agent or as dissolution medium at the crystallization stages

**[00204]** For example, purification can be carried out by means of a membrane distillation process. The membrane distillation process applied here occurs when two aqueous liquids with different temperatures are separated through a hydrophobic membrane. The driving force of the process was supplied by the partial pressure vapour difference caused by the temperature gradient between these solutions. Vapour travels from the warm to the cold side. Without wishing to be bound to such a theory, the separation mechanism was based on the vapour/liquid equilibrium of the HCl/water liquid mixture. Practical application of such a technology has been applied to HCl/water, $H_2SO_4$/water systems and also on large commercial scales on aqueous solution of sodium chloride with the purpose of obtaining potable water from seawater and nano water production. Therefore membrane distillation was a separation process based on evaporation through a porous hydrophobic membrane. The process was performed at about 60°C and was effective to recover heat from the 104 and 102 stage with an internal water circulation loop, in order to maintain a constant incoming temperature to the membranes. For example, eight membranes of 300,000 $m^2$ equivalent surface area can be used per membrane to obtain a concentration of HCl well above the azeotropic point (i.e. > 36%) of the ≈ 750 $m^3$/h and final 90% concentration is then obtained through pressure distillation (rectification column).

**[00205]** Purification of HCl by processing thus regenerated acid through hydrophobic membrane and separating water from HCl; therefore increasing HCl concentration up to about 36% (above azeotropic point) and therefore allowing with a single stage of rectification through a pressure stripping column to obtain >90% in gaseous phase, for crystallization stage (sparging); and therefore controlling acid concentration into crystallization stages up to 30-35 $\%_{(aq)}$.

**[00206]** As indicated stage 107 was operated at about 60°C and heat input provided by heat recovery from stages 102 to 110. Rectification column was operated at about 140°C in the reboiler part. Net energy requirement was neutral (negative in fact at -3.5 Gj/t $Al_2O_3$) since both systems were in equilibrium and in balance.

[00207] For example, the acid purification can be carried out by using adsorption technology over an activated alumina bed. In continuous mode, at least two adsorption columns are required to achieve either adsorption in one of them and regeneration in the other one. Regeneration can be performed by feeding in counter-current a hot or depressurized gas. This technology will result in a purified gas at 100% wt.

[00208] For example, the acid purification can be made by using calcium chloride as entrainer of water. A lean hydrochloric acid solution is contacted with a strong calcium chloride solution through a column. The water is then removed from the hydrochloric acid solution and 99.9% gaseous HCl comes out of the process. Cooling water and cryogenic coolant is used to condense water traces in the HCl. The weak $CaCl_2$ solution is concentrated by an evaporator that ensures the recuperation of calcium chloride. Depending on the impurities in the incoming HCl solution feed to the column, some metals can contaminate the calcium chloride concentrated solution. A precipitation with $Ca(OH)_2$ and a filtration allows the removal of those impurities. The column can operate for example at 0.5 barg. This technology can allow for the recuperation of 98% of the HCl.

[00209] Table 7 shows the results obtained concerning the process shown in Fig. 6.

| Composition (% wt) | Stage 101 Yield (%) | Stage 102 Yield (%) | Stage 106 Yield (%) | Stage 105 Yield (%) | MgO tpy | MgO Yield (%) | Stage 107 Yield (%) | Stage 108 Yield (%) | TOTAL PRODUCED Yield (%) |
|---|---|---|---|---|---|---|---|---|---|
| ***Main constituents*** | | | | | | | | | |
| $SiO_2$ | --- | 99.997% | --- | --- | --- | --- | --- | --- | 99.997% |
| Al | --- | 98.02% | 95.03% | --- | --- | --- | --- | --- | 95.03% |
| Fe | --- | 100.00% | --- | 92.65% | --- | --- | --- | --- | 92.65% |
| Mg | --- | 99.998% | --- | --- | 29,756 | 92.64% | --- | --- | 92.64% |
| Ca | --- | 99.998% | --- | --- | --- | --- | --- | --- | 98.28% |
| Na | --- | 99.998% | --- | --- | --- | --- | --- | --- | 92.76% |
| K | --- | 100.00% | --- | --- | --- | --- | --- | --- | 93.97% |
| Others incl. $H_2O$ | --- | | --- | --- | --- | --- | --- | --- | --- |
| RE/RM | --- | 99.80% | --- | 92.32% | --- | --- | --- | 84.67% | 84.67% |
| ***By-Products*** | | | | | | | | | |
| NaOH | --- | --- | --- | --- | 68,556 | --- | --- | --- | --- |
| NaOCl | --- | --- | --- | --- | 9,269 | --- | --- | --- | --- |
| KOH | --- | --- | --- | --- | 73,211 | --- | --- | --- | --- |
| KOCl | --- | --- | --- | --- | 9,586 | --- | --- | --- | --- |
| $CaSO_4$ | --- | --- | --- | --- | 46,837 | --- | --- | --- | --- |
| ***Reactants*** | | | | | | | | | |
| $H_2SO_4$ (*) | --- | --- | --- | --- | 19,204 | --- | --- | --- | --- |
| Fresh HCl M-UP | --- | --- | --- | --- | --- | --- | 99.75% | --- | 99.75% |
| Total | --- | 98.55% | 95.03% | | 256,419 | 92.64% | 99.75% | 84.67% | |

**[00210]** Tables 8 to 26 show results obtained concerning the products made in accordance with the process shown in Fig. 6 in comparison with standard of the industry.

Table 8.

| Chemical composition of obtained alumina | | |
|---|---|---|
| Element | % Weight* | Standard used in industry |
| $Al_2O_3$ | 99.938 | 98.35 min |
| $Fe_2O_3$ | 0.0033 | 0.0100 |
| $SiO_2$ | 0.0032 | 0.0150 |
| $TiO_2$ | 0.0003 | 0.0030 |
| $V_2O_5$ | 0.0008 | 0.0020 |
| ZnO | 0.0005 | 0.0030 |
| $Cr_2O_3$ | 0.0003 | N/A |
| MgO | 0.0090 | N/A |
| MnO | 0.0002 | N/A |
| $P_2O_5$ | 0.0039 | 0.0010 |
| Cu | 0.0030 | N/A |
| Ca | 0.0020 | 0.0030 |
| Na | 0.0190 | 0.4000 |
| K | 0.0053 | 0.0150 |
| Li | 0.0009 | N/A |
| Ba | < 0.00001 | 0.0000 |
| Th | < 0.000001 | 0.0000 |
| U | < 0.000001 | 0.0000 |
| Free $Cl^-$ | Not detectable | 0.0000 |
| LOI | < 1.0000 | < 1.0000 |

Table 9.

| Physical properties of obtained alumina | | |
|---|---|---|
| Property | Orbite Alumina | Standard used in industry |
| PSD < 20µm | 5-10% | N/A |
| PSD < 45µm | 10-12% | < 10% |
| PSD > 75µm | 50-60% | N/A |
| SSA ($m^2/g$) | 60-85 | 60-80 |
| Att. Index | 10-12% | < 10% |
| α $Al_2O_3$ | 2-5% | < 7-9% |

Table 10.

| Chemical composition of obtained hematite | |
|---|---|
| Element | % Weight |
| $Fe_2O_3$ | > 99.5% |
| Hydrolysable elements | < 0.2% |

Table 11.

| Physical properties of obtained hematite* | |
|---|---|
| Property | Orbite hematite |
| $PSD_{mean}$ | 25-35 µm |
| Density (bulk) | 2000-3000 $kg/m^3$ |
| Humidity after filtration | < 10% |

* Material can be produced as brickets

Table 12.

| Chemical composition of obtained silica | |
|---|---|
| Element | % Weight |
| $SiO_2$ | > 99.7 |
| $Al_2O_3$ | < 0.25% |
| MgO | ≈ 0.1% |
| $Fe_2O_3$ | ≈ 0.1% |
| CaO | ≈ 0.01% |
| $Na_2O$ | < 0.1% |
| $K_2O$ | < 0.1% |

**Note:** Product may have unbleached cellulose fiber filter aid. Cellulose wood flour.

Table 13.

| Physical properties of obtained silica | |
|---|---|
| Property | Orbite silica |
| $PSD_{mean}$ | 10-20 μm |
| Specific surface area | 34 $m^2/g$ |
| Density (bulk) | 2000-2500 $kg/m^3$ |
| Humidity after filtration | < 40% |

Table 14.

| Purity of obtained rare earth element oxides | |
|---|---|
| Element | Purity (%) |
| $Ga_2O_3$ | > 99% |
| $Sc_2O_3$ | |
| $Y_2O_3$ | |
| $La_2O_3$ | |
| $Ce_2O_3$ | |
| $Pr_2O_3$ | |
| $Nd_2O_3$ | |
| $Sm_2O_3$ | |
| $Eu_2O_3$ | |
| $Gd_2O_3$ | |
| $Dy_2O_3$ | |
| $Er_2O_3$ | |
| Physical properties of obtained REE-O/RM-O | |
| Property | Orbite REE-O/RM-O |
| $PSD_{mean}$ | 2-30 μm |
| Density | 5500-13000 $kg/m^3$ |
| LOI | < 1% |

Table 15.

| Chemical composition of obtained MgO | | |
|---|---|---|
| Element | Typical | Specification |
| MgO | $99.0^+$ | 98.35min |
| CaO | 0.0020 | 0.83 |
| $SiO_2$ | 0.0000 | 0.20 max |
| $B_2O_3$ | 0.0000 | 0.02 max |
| $Al_2O_3$ | 0.0300 | 0.12 max |
| $Fe_2O_3$ | 0.0160 | 0.57 max |
| $MnO_2$ | < 0.14 | 0.14 max |
| LOI | 0.7% | < 1% |

Table 16.

| Physical properties of obtained MgO | |
|---|---|
| Property | Orbite MgO |
| $PSD_{mean}$ | 10 µm |
| Density | N/A |
| LOI | 650 kg/m³ |

Table 17.

| Chemical composition of obtained NaOH | |
|---|---|
| Element | % Weight |
| Sodium hydroxide | 32% |
| Water | 68% |

Table 18.

| Physical properties of obtained NaOH | |
|---|---|
| Property | Sodium hydroxide (NaOH) |
| Physical state | Liquid |
| Vapour pressure | 14 mmHg |
| Viscosity | > 1 |
| Boiling point | 100°C |
| Melting point | 0°C |
| Specific gravity | 1.0 |

Table 19.

| Chemical composition of obtained sodium hypochlorite (bleach) | |
|---|---|
| Element | % Weight |
| Sodium hypochlorite | 12% |
| Sodium hydroxide | < 1% |
| Water | > 80% |

Table 20.

| Physical properties of obtained NaOCl | |
|---|---|
| Property | Sodium hypochlorite (NaOCl) |
| Physical state | Liquid |
| Vapour pressure | 1.6 kPa |
| Viscosity | N/A |
| Boiling point | 100 °C |
| Melting point | -3 °C |
| Specific gravity | 1.2 |

Table 21.

| Chemical composition of obtained potassium hydroxide | |
|---|---|
| Element | % Weight |
| Potassium hydroxide | 32% |
| Water | 68% |

Table 22.

| Physical properties of obtained potassium hydroxide | |
|---|---|
| Property | KOH |
| Physical state | Liquid |
| Vapour pressure | 17.5 mmHg |
| Viscosity | N/A |
| Boiling point | 100 °C |
| Melting point | N/A |
| Specific gravity | 1.18 |

Table 23.

| Chemical composition of obtained potassium hypochlorite (KOCl) | |
|---|---|
| Element | % Weight |
| Potassium hypochlorite | 12% |
| Potassium hydroxide | < 1% |
| Water | > 80% |

Table 24.

| Physical properties of obtained potassium hypochlorite | |
|---|---|
| Property | KOCl |
| Physical state | Liquid |
| Vapour pressure | N/A |
| Viscosity | N/A |
| Boiling point | 103 °C |
| Melting point | N/A |
| Specific gravity | > 1.0 |

Table 25.

| Chemical composition of obtained calcium sulphate dihydrate | |
|---|---|
| Element | % Weight |
| Calcium sulphate dihydrate | 100% |

Table 26.

| Physical properties of obtained calcium sulphate dihydrate | |
|---|---|
| Property | Orbite $CaSO_4 \cdot 2H_2O$ |
| Physical state | Solid |
| Specific gravity | 2.32 |

**[00211]** The processes of the present disclosure provide a plurality of important advantages and distinction over the known processes

**[00212]** The processes of the present disclosure provide fully continuous and economical solutions that can successfully extract alumina from various type of materials while providing ultra pure secondary products of high added value including highly concentrated rare earth elements and rare metals. The technology described in the present disclosure allows for an innovative amount of total acid recovery and also for a ultra high concentration of recovered acid. When combing it to the fact that combined with a semi-continuous leaching approach that favors very high extraction yields and allows a specific method of crystallization of the aluminum chloride and concentration of other value added elements. These processes also allow for preparing aluminum with such a produced alumina.

**[00213]** Specifically through the type of equipment used (for example vertical roller mill) and its specific operation, raw material grinding, drying and classifying can be applicable to various kinds of material hardness (furnace slag for example), various types of humidity (up to 30%) and incoming particle sizes. The particle size established provides the advantage, at the leaching stage, of allowing optimal contact between the minerals and the acid and then allowing faster kinetics of reaction. Particles size employed reduces drastically the abrasion issue and allows for the use of a simplified metallurgy/lining when in contact with hydrochloric acid.

[00214] A further advantage of the processes of the present disclosure is the combined high temperature and high incoming hydrochloric acid concentration. Combined with a semi continuous operation where the free HCl driving force is used systematically, iron and aluminum extraction yields do respectively reach 100% and 98% in less than about 40 % of the reference time of a basic batch process. Another advantage of higher HCl concentration than the concentration at azeotropic point is the potential of capacity increase. Again a higher HCl concentration than the concentration of HCl at the azeotropic point and the semi-continuous approach represent a substantial advance in the art.

[00215] Another advantage in that technique used for the mother liquor separation from the silica after the leaching stage countercurrent wash, is that band filters provide ultra pure silica with expected purity exceeding 96%.

[00216] The crystallization of $AlCl_3$ into $AlCl_3 \bullet 6H_2O$ using dried, cleaned and highly concentrated gaseous HCl as the sparging agent allows for a pure aluminum chloride hexahydrate with only few parts per million of iron and other impurities. A minimal number of stages are required to allow proper crystal growth.

[00217] The direct interconnection with the calcination of $AlCl_3 \bullet 6H_2O$ into $Al_2O_3$ which does produce very high concentration of gas allows the exact adjustment in continuous of the HCl concentration within the crystallizer and thus proper control of the crystal growth and crystallization process.

[00218] The applicants have now discovered fully integrated and continuous processes with substantially total hydrochloric acid recovery for the extraction of alumina and other value added products from various materials that contain aluminum (clay, bauxite, aluminosilicate materials, slag, red mud, fly ashes etc.) containing aluminum. In fact, the processes allows for the production of substantially pure alumina and other value added products purified such as purified silica, pure hematite, pure other minerals (ex: magnesium oxide) and

rare earth elements products. In addition, the processes do not require thermal pre-treatment before the acid leach operation. Acid leach is carried out using semi-continuous techniques with high pressure and temperature conditions and very high regenerated hydrochloric acid concentration. In addition, the processes do not generate any residues not sellable, thus eliminating harmful residues to environment like in the case of alkaline processes.

**[00219]** The advantage of the high temperature calcination stage, in addition for allowing to control the α-form of alumina required, is effective for providing a concentration of hydrochloric acid in the aqueous form (>38%) that is higher than the concentration of HCl at the azeotropic point and thus providing a higher incoming HCl concentration to the leaching stage. The calcination stage hydrochloric acid network can be interconnected to two (2) crystallization systems and by pressure regulation excess HCl can be being absorbed at the highest possible aqueous concentration. The advantage of having a hexahydrate chloride with low moisture content (< 2%) incoming feed allows for a continuous basis to recover acid at a concentration that is higher than the azeotropic concentration. This HCl balance and double usage into three (3) common parts of the processes and above azeotropic point is a substantial advance in the art.

**[00220]** Another advantage is the use of the incoming chemistry (ferric chloride) to the iron oxide and hydrochloric acid recovery unit where all excess heat load from any calcination part, pyrohydrolysis and leaching part is being recovered to preconcentrate the mother liquor in metal chloride, thus allowing, at very low temperature, the hydrolysis of the ferric chloride in the form of very pure hematite and the acid regeneration at the same concentration than at its azeotropic point.

**[00221]** A further major advantage of the instant process at the ferric chloride hydrolysis step is the possibility to concentrate rare earth elements in form of chlorides at very high concentration within the hydrolyser reactor through an internal loop between hydrolyzer and crystallization. The advantage in that the processes of the present disclosure benefit from the various steps where gradual concentration ratios are applied. Thus, at this stage, in addition to an internal concentration loop, having the silica, the aluminum, the iron and having in equilibrium a solution close to saturation (large amount of water evaporated, no presence of free hydrochloric acid) allows for taking rare earth elements and non-hydrolysable elements in parts per million into the incoming feed and to concentrate them in high percentage directly at the hydrolyser after ferric chloride removal Purification of the specific oxides (RE-O) can then be performed using various techniques when in percentage levels. The advantage is doubled here: concentration at very high level of rare earth elements using integrated process stages and most importantly the approach prevents from having the main stream (very diluted) of spent acid after the leaching step with the risk of contaminating the main aluminum chloride stream and thus affecting yields in $Al_2O_3$. Another important improvement of the art is that on top of being fully integrated, selective removal of components allows for the concentration of rare earth elements to relatively high concentration (percentages).

**[00222]** Another advantage of the process is again a selective crystallization of $MgCl_2$ through the sparging of HCl from either the alumina calcination step or the magnesium oxide direct calcination where in both cases highly concentrated acid both in gaseous phase or in aqueous form are being generated. As per aluminum chloride specific crystallization, the direct interconnection with the calcination reactor, the HCl gas very high concentration (about 85 to about 95 %, about 90 to 95 % or about 90 % by weight) allows for exact adjustment in continuous of the crystallizer based on quality of magnesium oxide targeted. Should this process step (MgO production or other value added metal oxide) be required based on incoming process feed chemistry, the rare earth elements extraction point then be done after this additional step; the advantage being the extra concentration effect applied.

**[00223]** The pyrohydrolysis allows for the final conversion of any remaining chloride and the production of refined oxides that can be used (in case of clay as starting material) as a fertilizer and allowing the processing of large amount of wash water from the processes with the recovery hydrochloric acid in close loop at the azeotropic point for the leaching step. The advantage of this last step is related to the fact that it does totally close the process loop in terms of acid recovery and the insurance that no residues harmful to the environment are being generated while processing any type of raw material, as previously described.

**[00224]** A major contribution to the art is that the proposed fully integrated processes of the present disclosure is really allowing, among others, the processing of bauxite in an economic way while generating no red mud or harmful residues. In addition to the fact of being applicable to other natural of raw materials (any suitable aluminum-containing material or aluminous ores), the fact of using hydrochloric acid total recovery and a global concentration that is higher than the concentration at the azeotropic point (for example about 21% to about 38%), the selective extraction of value added secondary products and compliance (while remaining highly competitive on transformation cost) with environmental requirements, represent major advantages in the art.

**[00225]** It was thus demonstrated that the present disclosure provides fully integrated processes for the preparation of pure aluminum oxide using a hydrochloric acid treatment while producing high purity and high quality products (minerals) and extracting rare earth elements and rare metals.

**[00226]** With respect to the above-mentioned examples 1 to 5, the person skilled in the art will also understand that depending on the starting material used i.e. argillite, bauxite, kaolin, nepheline, aluminosilicate materials, red mud, slag, fly ashes, industrial refractory materials etc., some parameters might need to be adjusted consequently. In fact, for example, certain parameters such as reaction time, concentration, temperature may vary in accordance with the reactivity of the selected starting material (aluminum-containing material).

**[00227]** While a description was made with particular reference to the specific embodiments, it will be understood that numerous modifications thereto will appear to those skilled in the art. Accordingly, the above description and accompanying drawings should be taken as specific examples and not in a limiting sense.

**WHAT IS CLAIMED IS:**

1. A process for preparing alumina, said process comprising :

leaching an aluminum-containing material with HCl so as to obtain a leachate comprising aluminum ions and a solid, and separating said solid from said leachate;

reacting said leachate with HCl so as to obtain a liquid and a precipitate comprising said aluminum ions in the form of $AlCl_3$, and separating said precipitate from said liquid; and

heating said precipitate under conditions effective for converting $AlCl_3$ into $Al_2O_3$ and optionally recovering gaseous HCl so-produced.

2. The process of claim 1, wherein said aluminum-containing material is leached with HCl having a concentration of about 25 to about 45 weight %.

3. The process of claim 1, wherein said aluminum-containing material is leached with HCl having a concentration of about 25 to about 45 weight % at a temperature of about 125 to about 225 °C.

4. The process of claim 1, wherein said aluminum-containing material is leached with HCl having a concentration of about 25 to about 45 weight % at a temperature of about 160 to about 190 °C.

5. The process of claim 1, wherein said aluminum-containing material is leached with HCl having a concentration of about 25 to about 45 weight % at a temperature of about 160 to about 175 °C.

6. The process of claim 1, wherein said aluminum-containing material is leached with HCl having a concentration of about 25 to about 45 weight % at a temperature of about 185 to about 190 °C.

7. The process of claim 1, wherein said aluminum-containing material is leached with HCl having a concentration of about 18 to about 45 weight %.

8. The process of claim 1, wherein said aluminum-containing material is leached with HCl having a concentration of about 18 to about 45 weight % at a temperature of about 125 to about 225 °C.

9. The process of claim 1, wherein said aluminum-containing material is leached with HCl having a concentration of about 18 to about 45 weight % at a temperature of about 160 to about 190 °C.

10. The process of claim 1, wherein said aluminum-containing material is leached with HCl having a concentration of about 18 to about 45 weight % at a temperature of about 160 to about 175 °C.

11. The process of claim 1, wherein said aluminum-containing material is leached with HCl having a concentration of about 18 to about 45 weight % at a temperature of about 185 to about 190 °C.

12. The process of claim 1, wherein said aluminum-containing material is leached with HCl having a concentration of about 18 to about 32 weight % at a temperature of about 125 to about 225 °C.

13. The process of claim 1, wherein said aluminum-containing material is leached with HCl having a concentration of about 18 to about 32 weight % at a temperature of about 160 to about 190 °C.

14. The process of claim 1, wherein said aluminum-containing material is leached with HCl having a concentration of about 18 to about 32 weight % at a temperature of about 160 to about 175 °C.

15. The process of claim 1, wherein said aluminum-containing material is leached with HCl having a concentration of about 18 to about 32 weight % at a temperature of about 185 to about 190 °C.

16. The process of any one of claims 1 to 15, wherein said process further comprises recycling said gaseous HCl so-produced by contacting it with water so as to obtain a composition having a concentration of about 25 to about 45 weight % and using said composition for leaching said aluminum-containing material.

17. The process of claim 16, wherein said recycled gaseous HCl so-produced is contacted with water so as to obtain said composition having a concentration of about 26 to about 42 weight % and said composition is reacted, at a temperature of about 125 to about 225 °C, with said aluminum-containing material so as to leaching it.

18. The process of claim 16, wherein said recycled gaseous HCl so-produced is contacted with water so as to obtain said composition having a concentration of about 28 to about 40 weight % and said composition is reacted, at a temperature of about 150 to about 200 °C, with said aluminum-containing material so as to leaching it.

19. The process of claim 16, wherein said recycled gaseous HCl so-produced is contacted with water so as to obtain said composition having a concentration of about 30 to about 38 weight % and said composition is reacted, at a temperature of about 150 to about 200 °C, with said aluminum-containing material so as to leaching it.

20. The process claim 19, wherein said recycled gaseous HCl so-produced is contacted with water so as to obtain said composition having a concentration between 18 and 36 weight %.

21. The process claim 19, wherein said recycled gaseous HCl so-produced is contacted with water so as to obtain said composition having a concentration between 25 and 36 weight %.

22. The process of claim 19, wherein said composition is reacted, at a temperature of about 160 to about 180 °C with said aluminum-containing material so as to leaching it.

23. The process of claim 19, wherein said composition is reacted, at a temperature of about 160 to about 175 °C with said aluminum-containing material so as to leaching it.

24. The process of claim 19, wherein said composition is reacted, at a temperature of about 165 to about 170 °C with said aluminum-containing material so as to leaching it.

25. The process of any one of claims 1 to 24, wherein said liquid comprises at least one iron chloride.

26. The process of claim 25, wherein said at least one iron chloride is $FeCl_2$, $FeCl_3$ or a mixture thereof.

27. The process of claim 25 or 26, wherein said liquid is concentrated to a concentrated liquid having a concentration of said at least one iron chloride of at least 30% by weight; and then hydrolyzed at a temperature of about 155 to about 350 °C.

28. The process of claim 25 or 26, wherein said liquid is concentrated to a concentrated liquid having a concentration of said at least one iron

iron chloride of at least 30% by weight; and then said at least one iron chloride is hydrolyzed at a temperature of about 155 to about 350 °C while maintaining a ferric chloride concentration at a level of at least 65% by weight, to generate a composition comprising a liquid and precipitated hematite, and recovering said hematite.

29. The process of claim 25 or 26, wherein said at least one iron chloride is hydrolyzed at a temperature of about 165 to about 170 °C.

30. The process of claim 25 or 26, wherein said liquid is concentrated to a concentrated liquid having a concentration of said at least one iron chloride of at least 30% by weight; and then said at least one iron chloride is hydrolyzed at a temperature of about 155 to about 350 °C while maintaining a ferric chloride concentration at a level of at least 65% by weight, to generate a composition comprising a liquid and precipitated hematite; recovering said hematite; and recovering rare earth elements and/or rare metals from said liquid.

31. The process of claim 30, wherein said at least one iron chloride is hydrolyzed at a temperature of about 155 to about 170 °C.

32. The process of claim 30 or 31, further comprising, after recovery of said rare earth elements and/or said rare metals, reacting said liquid with HCl so as to cause precipitation of $MgCl_2$, and recovering same.

33. The process of claim 30 or 31, further comprising calcining $MgCl_2$ into MgO.

34. The process of claim 30 or 31, further comprising calcining $MgCl_2$ into MgO and recycling the gaseous HCl so-produced by contacting it with water so as to obtain a composition having a concentration of about 25 to about 45 weight % and using said composition for leaching said aluminum-containing material.

35. The process of claim 30 or 31, further comprising calcining $MgCl_2$ into MgO and recycling the gaseous HCl so-produced by contacting it with water so as to obtain a composition having a concentration of about 18 to about 45 weight % and using said composition for leaching said aluminum-containing material.

36. The process of any one of claims 30 to 35, further comprising, downstream of recovery of said rare earth elements and/or rare metals, recovering NaCl from said liquid, reacting said NaCl with $H_2SO_4$, and substantially selectively precipitating $Na_2SO_4$.

37. The process of any one of claims 30 to 36, further comprising, downstream of recovery of said rare earth elements and/or rare metals, recovering KCl from said liquid, reacting said KCl with $H_2SO_4$, and substantially selectively precipitating $K_2SO_4$.

38. The process of any one of claims 30 to 35, further comprising, downstream of recovery of said rare earth elements and/or rare metals, recovering NaCl from said liquid, carrying out an electrolysis to generate NaOH and NaOCl.

39. The process of any one of claims 30 to 35 and 38, further comprising, downstream of recovery of said rare earth elements and/or rare metals, recovering KCl from said liquid, reacting said KCl, carrying out an electrolysis to generate KOH and KOCl.

40. The process of claim 25 or 26, wherein said liquid is concentrated to a concentrated liquid having a concentration of said at least one iron chloride of at least 30% by weight; and then said at least one iron chloride is hydrolyzed at a temperature of about 155 to about 350 °C while maintaining a ferric chloride concentration at a level of at least 65% by weight, to generate a composition comprising a liquid and

precipitated hematite; recovering said hematite; and extracting NaCl and/or KCl from said liquid.

41. The process of claim 40, further comprising reacting said NaCl with $H_2SO_4$ so as to substantially selectively precipitate $Na_2SO_4$.

42. The process of claim 40, further comprising reacting said KCl with $H_2SO_4$ so as to substantially selectively precipitate $K_2SO_4$.

43. The process of claim 40, further comprising carrying out an electrolysis of said NaCl to generate NaOH and NaOCl.

44. The process of claim 40, further comprising carrying out an electrolysis of aid KCl to generate KOH and KOCl.

45. The process of any one of claims 1 to 44, wherein said process comprises separating said solid from said leachate and washing said solid so as to obtain silica having a purity of at least 95 %.

46. The process of any one of claims 1 to 44, wherein said process comprises separating said solid from said leachate and washing said solid so as to obtain silica having a purity of at least 98 %.

47. The process of any one of claims 1 to 44, wherein said process comprises separating said solid from said leachate and washing said solid so as to obtain silica having a purity of at least 99 %.

48. The process of any one of claims 1 to 47, wherein said process comprises reacting said leachate with gaseous HCl so as to obtain said liquid and said precipitate comprising said aluminum ions, said precipitate being formed by crystallization of $AlCl_3 \bullet 6H_2O$.

49. The process of any one of claims 1 to 47, wherein said process comprises reacting said leachate with dry gaseous HCl so as to obtain said liquid and said precipitate comprising said aluminum ions, said precipitate being formed by crystallization of $AlCl_3{\bullet}6H_2O$.

50. The process of claim 48 or 49, wherein said gaseous HCl has a HCl concentration of at least 85 % by weight.

51. The process of claim 48 or 49, wherein said gaseous HCl has a HCl concentration of at least 90 % by weight.

52. The process of claim 48 or 49, wherein said gaseous HCl has a HCl concentration of about 90 % by weight.

53. The process of claim 48 or 49, wherein said gaseous HCl has a concentration of about 90 % to about 95 % by weight.

54. The process of any one of claims 48 to 53, wherein during said crystallization of $AlCl_3{\bullet}6H_2O$, said liquid is maintained at a concentration of HCl of about 25 to about 35 % by weight.

55. The process of any one of claims 48 to 53, wherein during said crystallization of $AlCl_3{\bullet}6H_2O$, said liquid is maintained at a concentration of HCl of about 30 to about 32 % by weight.

56. The process of any one of claims 48 to 55, wherein said HCl is obtained from said gaseous HCl so-produced.

57. The process of any one of claims 1 to 56, wherein said process comprises reacting said leachate with HCl recovered during said processs and ahaving a concentration of at least 30 % as to obtain said liquid and said precipitate comprising said aluminum ions, said precipitate being formed by crystallization of $AlCl_3{\bullet}6H_2O$.

58. The process of any one of claims 48 to 57, wherein said crystallization is carried out at a temperature of about 45 to about 65 °C.

59. The process of any one of claims 48 to 57, wherein said crystallization is carried out at a temperature of about 50 to about 60 °C.

60. The process of any one of claims 1 to 59, wherein said process comprises converting $AlCl_3•6H_2O$ into $Al_2O_3$ by carrying out a calcination of $AlCl_3•6H_2O$.

61. The process of any one of claims 1 to 60, wherein said process comprises heating said precipitate at a temperature of at least 1200 °C for converting $AlCl_3•6H_2O$ into $Al_2O_3$.

62. The process of any one of claims 1 to 60, wherein said process comprises heating said precipitate at a temperature of at least 1250 °C for converting $AlCl_3•6H_2O$ into $Al_2O_3$.

63. The process of any one of claims 1 to 60, wherein said process comprises heating said precipitate at a temperature of at least 900 °C for converting $AlCl_3•6H_2O$ into $Al_2O_3$.

64. The process of any one of claims 1 to 63, wherein said process comprises converting $AlCl_3•6H_2O$ into alpha-$Al_2O_3$.

65. The process of any one of claims 1 to 60, wherein said process comprises heating said precipitate at a temperature of at least 350 °C for converting $AlCl_3•6H_2O$ into $Al_2O_3$.

66. The process of any one of claims 1 to 60, wherein said process comprises heating said precipitate at a temperature of about 350 °C to about 500 °C for converting $AlCl_3•6H_2O$ into $Al_2O_3$.

67. The process of any one of claims 1 to 60, wherein said process comprises heating said precipitate at a temperature of about 375 °C to about 450 °C for converting $AlCl_3•6H_2O$ into $Al_2O_3$.

68. The process of any one of claims 1 to 60, wherein said process comprises heating said precipitate at a temperature of about 375 °C to about 425 °C for converting $AlCl_3•6H_2O$ into $Al_2O_3$.

69. The process of any one of claims 1 to 60, wherein said process comprises heating said precipitate at a temperature of about 385 °C to about 400 °C for converting $AlCl_3•6H_2O$ into $Al_2O_3$.

70. The process of any one of claims 66 to 70, wherein said process comprises converting $AlCl_3•6H_2O$ into beta-$Al_2O_3$.

71. The process of any one of claims 1 to 70, wherein converting $AlCl_3•6H_2O$ into $Al_2O_3$ comprises carrying out a calcination via a two-stage circulating fluid bed reactor.

72. The process of any one of claims 1 to 70, wherein converting $AlCl_3•6H_2O$ into $Al_2O_3$ comprises carrying out a calcination via a two-stage circulating fluid bed reactor that comprises a preheating system.

73. The process of claim 72, wherein said preheating system comprises a plasma torch.

74. The process of claim 73, wherein said plasma torch is effective for preheating air entering into a calcination reactor.

75. The process of claim 73, wherein said plasma torch is effective for generating steam that is injected into a calcination reactor.

76. The process of claim 73, wherein said plasma torch is effective for generating steam that is as fluidization medium in a fluid bed reactor.

77. The process of process of any one of claims 1 to 76, wherein converting $AlCl_3•6H_2O$ into $Al_2O_3$ comprises carrying out a one-step calcination.

78. The process of process of any one of claims 1 to 77, wherein said process comprises converting $AlCl_3•6H_2O$ into $Al_2O_3$ by carrying out a calcination of $AlCl_3•6H_2O$, said calcination comprising steam injection.

79. The process of claim 78, wherein steam is injected at a pressure of about 200 to about 700 psig.

80. The process of claim 78, wherein steam is injected at a pressure of about 300 to about 700 psig.

81. The process of claim 78, wherein steam is injected at a pressure of about 400 to about 700 psig.

82. The process of claim 78, wherein steam is injected at a pressure of about 550 to about 650 psig.

83. The process of claim 78, wherein steam is injected at a pressure of about 575 to about 625 psig.

84. The process of claim 78, wherein steam is injected at a pressure of about 590 to about 610 psig.

85. The process of any one of claims 78 to 84, wherein steam is injected and a plasma torch is used for carrying fluidization.

86. The process of any one of claims 78 to 84, wherein steam is injected and a plasma torch is used for carrying fluidization.

87. The process of any one of claims 78 to 86, wherein said steam is overheated.

88. The process of any one of claims 1 to 87, wherein said process comprises converting $AlCl_3 \bullet 6H_2O$ into $Al_2O_3$ by carrying out a calcination of $AlCl_3 \bullet 6H_2O$ in which is provided by the combustion of a fossil fuel, carbon monoxide, propane, natural gas, a Refinery Fuel Gas, coal, or chlorinated gases and/or solvants.

89. The process of any one of claims 1 to 87, wherein said process comprises converting $AlCl_3 \bullet 6H_2O$ into $Al_2O_3$ by carrying out a calcination of $AlCl_3 \bullet 6H_2O$ that is provided by the combustion of gas mixture that is a an incoming smelter gas or a reducer offgas.

90. The process of any one of claims 1 to 87, wherein said process comprises converting $AlCl_3 \bullet 6H_2O$ into $Al_2O_3$ by carrying out a calcination of $AlCl_3 \bullet 6H_2O$ that is provided by the combustion of gas mixture that comprises :

$CH_4$ : 0 to about 1% vol;

$C_2H_6$ : 0 to about 2% vol;

$C_3H_8$ : 0 to about 2% vol;

$C_4H_{10}$ : 0 to about 1% vol;

$N_2$ : 0 to about 0.5% vol;

$H_2$ : about 0.25 to about 15.1 % vol;

CO : about 70 to about 82.5 % vol; and

$CO_2$ : about 1.0 to about 3.5% vol.

91. The process of claim 90, wherein $O_2$ is substantially absent from said mixture.

92. The process of any one of claims 1 to 87, wherein said process comprises converting $AlCl_3•6H_2O$ into $Al_2O_3$ by carrying out a calcination of $AlCl_3•6H_2O$ in which is provided by electric heating, gas heating, microwave heating.

93. The process of any one of claims 1 to 92, wherein converting $AlCl_3•6H_2O$ into $Al_2O_3$ comprises carrying out a calcination by means of fluid bed reactor.

94. The process of claim 93, wherein the fluid bed reactor comprises a metal catalyst chosen from metal chlorides.

95. The process of claim 93, wherein the fluid bed reactor comprises $FeCl_3$, $FeCl_2$ or a mixture thereof.

96. The process of claim 93, wherein the fluid bed reactor comprises $FeCl_3$.

97. The process of any one of claims 1 to 96, wherein said process is a semi-continuous process.

98. The process of any one of claims 1 to 96, wherein said process is a continuous process.

99. The process of any one of claims 1 to 98, wherein said process is effective for providing an $Al_2O_3$ recovery yield of at least 93 %.

100. The process of any one of claims 1 to 98, wherein said process is effective for providing an $Al_2O_3$ recovery yield of about 90 % to about 95 %.

101. The process of any one of claims 1 to 100, wherein said process is effective for providing a $Fe_2O_3$ recovery yield of at least 98 %.

102. The process of any one of claims 1 to 100, wherein said process is effective for providing a $Fe_2O_3$ recovery yield of about 98 % to about 99.5 %.

103. The process of any one of claims 1 to 102, wherein said process is effective for providing a MgO recovery yield of at least 96 %.

104. The process of any one of claims 1 to 102, wherein said process is effective for providing a MgO recovery yield of about 96 to about 98 %.

105. The process of any one of claims 1 to 104, wherein said process is effective for providing a HCl recovery yield of at least 98 %.

106. The process of any one of claims 1 to 104, wherein said process is effective for providing a HCl recovery yield of at least 99 %.

107. The process of any one of claims 1 to 104, wherein said process is effective for providing a HCl recovery yield of about 98 to about 99.9 %.

108. The process of any one of claims 1 to 107, wherein said aluminum-containing material is leached at a pressure of about 4 to about 10 barg.

109. The process of any one of claims 1 to 107, wherein said aluminum-containing material is leached at a pressure of about 4 to about 8 barg.

110. The process of any one of claims 1 to 107, wherein said aluminum-containing material is leached at a pressure of about 5 to about 6 barg.

111. The process of any one of claims 1 to 110, further comprising, before leaching said aluminum-containing material, a pre-leaching removal of fluorine optionally contained in said aluminum-containing material.

112. The process of any one of claims 1 to 111, comprising leaching said aluminum-containing material with HCl so as to obtain said leachate comprising aluminum ions and said solid, separating said solid from said leachate; and further treating said solid so as to separate $SiO_2$ from $TiO_2$ that are contained therein.

113. The process of any one of claims 1 to 111, comprising leaching said aluminum-containing material with HCl so as to obtain said leachate comprising aluminum ions and said solid, separating said solid from said leachate; and further treating said solid with HCl so as to separate $SiO_2$ from $TiO_2$ that are contained therein.

114. The process of any one of claims 1 to 111, comprising leaching said aluminum-containing material with HCl so as to obtain said leachate comprising aluminum ions and said solid, separating said solid from said leachate; and further treating said solid with HCl at a concentration of less than 20 % by weight, at a temperature of less than 85 $^{o}$C, in the presence of MgCl, so as to separate $SiO_2$ from $TiO_2$ that are contained therein.

115. The process of any one of claims 1 to 114, wherein said aluminum-containing material is chosen from aluminosilicate minerals.

116. The process of any one of claims 1 to 114, wherein said aluminum-containing material is argillite.

117. The process of any one of claims 1 to 114, wherein said aluminum-containing material is bauxite.

118. The process of any one of claims 1 to 114, wherein said aluminum-containing material is an industrial refractory material.

119. The process of any one of claims 1 to 114, wherein said aluminum-containing material is red mud.

120. The process of any one of claims 1 to 119, wherein said process is effective for avoiding producing red mud.

121. The process of any one of claims 1 to 120, wherein the recovered HCl is purified and/or concentrated.

122. The process of claim 121, wherein the recovered HCl is purified by means of a membrane distillation process.

123. The process of claim 121, wherein the recovered HCl is gaseous HCl and is treated with $H_2SO_4$ so as to reduce the amount of water present in the gaseous HCl.

124. The process of claim 123, wherein the recovered HCl is gaseous HCl and is passed through a packed column so as to be in contact with a $H_2SO_4$ countercurrent flow so as to reduce the amount of water present in the gaseous HCl.

125. The process of claim 124, wherein the column is packed with polypropylene or polytrimethylene terephthalate.

126. The process of any one of claims 121 and 123 to 125, wherein the concentration of gaseous HCl is increased by at least 50 %.

127. The process of any one of claims 121 and 123 to 125, wherein the concentration of gaseous HCl is increased by at least 60 %.

128. The process of any one of claims 121 and 123 to 125, wherein the concentration of gaseous HCl is increased by at least 70 %.

129. The process of claim 121, wherein the recovered HCl is gaseous HCl and is treated with $CaCl_2$ so as to reduce the amount of water present in the gaseous HCl.

130. The process of claim 129, wherein the recovered HCl is gaseous HCl and is passed through a column packed with $CaCl_2$ so as to reduce the amount of water present in the gaseous HCl.

131. The process of any one of claims 121 to 130, wherein the concentration of gaseous HCl is increased from a value below the azeotropic point before treatment to a value above the azeotropic point after treatment.

132. A process for preparing aluminum, said process comprising :

leaching an aluminum-containing material with HCl so as to obtain a leachate comprising aluminum ions and a solid, and separating said solid from said leachate;

reacting said leachate with HCl so as to obtain a liquid and a precipitate comprising said aluminum ions in the form of $AlCl_3$, and separating said precipitate from said liquid;

heating said precipitate under conditions effective for converting $AlCl_3$ into $Al_2O_3$ and optionally recovering gaseous HCl so-produced; and converting said $Al_2O_3$ into alumina.

133. The process of claim 132, wherein said aluminum-containing material is leached with HCl having a concentration of about 25 to about 45 weight %.

134. The process of claim 132, wherein said aluminum-containing material is leached with HCl having a concentration of about 25 to about 45 weight % at a temperature of about 125 to about 225 °C.

135. The process of claim 132, wherein said aluminum-containing material is leached with HCl having a concentration of about 25 to about 45 weight % at a temperature of about 160 to about 190 °C.

136. The process of claim 132, wherein said aluminum-containing material is leached with HCl having a concentration of about 25 to about 45 weight % at a temperature of about 160 to about 175 °C.

137. The process of claim 132, wherein said aluminum-containing material is leached with HCl having a concentration of about 25 to about 45 weight % at a temperature of about 185 to about 190 °C.

138. The process of claim 132, wherein said aluminum-containing material is leached with HCl having a concentration of about 18 to about 45 weight %.

139. The process of claim 132, wherein said aluminum-containing material is leached with HCl having a concentration of about 18 to about 45 weight % at a temperature of about 125 to about 225 °C.

140. The process of claim 132, wherein said aluminum-containing material is leached with HCl having a concentration of about 18 to about 45 weight % at a temperature of about 160 to about 190 °C.

141. The process of claim 132, wherein said aluminum-containing material is leached with HCl having a concentration of about 18 to about 45 weight % at a temperature of about 160 to about 175 °C.

142. The process of claim 132, wherein said aluminum-containing material is leached with HCl having a concentration of about 18 to about 45 weight % at a temperature of about 185 to about 190 °C.

143. The process of claim 132, wherein said aluminum-containing material is leached with HCl having a concentration of about 18 to about 32 weight % at a temperature of about 125 to about 225 °C.

144. The process of claim 132, wherein said aluminum-containing material is leached with HCl having a concentration of about 18 to about 32 weight % at a temperature of about 160 to about 190 °C.

145. The process of claim 132, wherein said aluminum-containing material is leached with HCl having a concentration of about 18 to about 32 weight % at a temperature of about 160 to about 175 °C.

146. The process of claim 132, wherein said aluminum-containing material is leached with HCl having a concentration of about 18 to about 32 weight % at a temperature of about 185 to about 190 °C.

147. The process of any one of claims 132 to 146, wherein said process further comprises recycling said gaseous HCl so-produced by contacting it with water so as to obtain a composition having a concentration of about 25 to about 45 weight % and using said composition for leaching said aluminum-containing material.

148. The process of claim 147, wherein said recycled gaseous HCl so-produced is contacted with water so as to obtain said composition having a concentration of about 26 to about 42 weight % and said

composition is reacted, at a temperature of about 125 to about 225 °C, with said aluminum-containing material so as to leaching it.

149. The process of claim 147, wherein said recycled gaseous HCl so-produced is contacted with water so as to obtain said composition having a concentration of about 28 to about 40 weight % and said composition is reacted, at a temperature of about 150 to about 200 °C, with said aluminum-containing material so as to leaching it.

150. The process of claim 147, wherein said recycled gaseous HCl so-produced is contacted with water so as to obtain said composition having a concentration of about 30 to about 38 weight % and said composition is reacted, at a temperature of about 150 to about 200 °C, with said aluminum-containing material so as to leaching it.

151. The process claim 150, wherein said recycled gaseous HCl so-produced is contacted with water so as to obtain said composition having a concentration between 18 and 36 weight %.

152. The process claim 150, wherein said recycled gaseous HCl so-produced is contacted with water so as to obtain said composition having a concentration between 25 and 36 weight %.

153. The process of claim 150, wherein said composition is reacted, at a temperature of about 160 to about 180 °C with said aluminum-containing material so as to leaching it.

154. The process of claim 150, wherein said composition is reacted, at a temperature of about 160 to about 175 °C with said aluminum-containing material so as to leaching it.

155. The process of claim 150, wherein said composition is reacted, at a temperature of about 165 to about 170 °C with said aluminum-containing material so as to leaching it.

156. The process of any one of claims 1 to 155, wherein said liquid comprises at least one iron chloride.

157. The process of claim 156, wherein said at least one iron chloride is $FeCl_2$, $FeCl_3$ or a mixture thereof.

158. The process of claim 156 or 157, wherein said liquid is concentrated to a concentrated liquid having a concentration of said at least one iron chloride of at least 30% by weight; and then hydrolyzed at a temperature of about 155 to about 350 °C.

159. The process of claim 156 or 157, wherein said liquid is concentrated to a concentrated liquid having a concentration of said at least one iron iron chloride of at least 30% by weight; and then said at least one iron chloride is hydrolyzed at a temperature of about 155 to about 350 °C while maintaining a ferric chloride concentration at a level of at least 65% by weight, to generate a composition comprising a liquid and precipitated hematite, and recovering said hematite.

160. The process of claim 156 or 157, wherein said at least one iron chloride is hydrolyzed at a temperature of about 165 to about 170 °C.

161. The process of claim 156 or 157, wherein said liquid is concentrated to a concentrated liquid having a concentration of said at least one iron chloride of at least 30% by weight; and then said at least one iron chloride is hydrolyzed at a temperature of about 155 to about 350 °C while maintaining a ferric chloride concentration at a level of at least 65% by weight, to generate a composition comprising a liquid and

precipitated hematite; recovering said hematite; and recovering rare earth elements and/or rare metals from said liquid.

162. The process of claim 161, wherein said at least one iron chloride is hydrolyzed at a temperature of about 155 to about 170 °C.

163. The process of claim 161 or 162, further comprising, after recovery of said rare earth elements and/or said rare metals, reacting said liquid with HCl so as to cause precipitation of $MgCl_2$, and recovering same.

164. The process of claim 162 or 163, further comprising calcining $MgCl_2$ into MgO.

165. The process of claim 163 or 164, further comprising calcining $MgCl_2$ into MgO and recycling the gaseous HCl so-produced by contacting it with water so as to obtain a composition having a concentration of about 25 to about 45 weight % and using said composition for leaching said aluminum-containing material.

166. The process of claim 163 or 164, further comprising calcining $MgCl_2$ into MgO and recycling the gaseous HCl so-produced by contacting it with water so as to obtain a composition having a concentration of about 18 to about 45 weight % and using said composition for leaching said aluminum-containing material.

167. The process of any one of claims 161 to 166, further comprising, downstream of recovery of said rare earth elements and/or rare metals, recovering NaCl from said liquid, reacting said NaCl with $H_2SO_4$, and substantially selectively precipitating $Na_2SO_4$.

168. The process of any one of claims 161 to 167, further comprising, downstream of recovery of said rare earth elements and/or rare metals, recovering KCl from said liquid, reacting said KCl with $H_2SO_4$, and substantially selectively precipitating $K_2SO_4$.

169. The process of any one of claims 161 to 166, further comprising, downstream of recovery of said rare earth elements and/or rare metals, recovering NaCl from said liquid, carrying out an electrolysis to generate NaOH and NaOCl.

170. The process of any one of claims 161 to 166 and 169, further comprising, downstream of recovery of said rare earth elements and/or rare metals, recovering KCl from said liquid, reacting said KCl, carrying out an electrolysis to generate KOH and KOCl.

171. The process of claim 156 or 157, wherein said liquid is concentrated to a concentrated liquid having a concentration of said at least one iron chloride of at least 30% by weight; and then said at least one iron chloride is hydrolyzed at a temperature of about 155 to about 350 °C while maintaining a ferric chloride concentration at a level of at least 65% by weight, to generate a composition comprising a liquid and precipitated hematite; recovering said hematite; and extracting NaCl and/or KCl from said liquid.

172. The process of claim 171, further comprising reacting said NaCl with $H_2SO_4$ so as to substantially selectively precipitate $Na_2SO_4$.

173. The process of claim 171, further comprising reacting said KCl with $H_2SO_4$ so as to substantially selectively precipitate $K_2SO_4$.

174. The process of claim 171, further comprising carrying out an electrolysis of said NaCl to generate NaOH and NaOCl.

175. The process of claim 171, further comprising carrying out an electrolysis of aid KCl to generate KOH and KOCl.

176. The process of any one of claims 132 to 175, wherein said process comprises separating said solid from said leachate and washing said solid so as to obtain silica having a purity of at least 95 %.

177. The process of any one of claims 132 to 175, wherein said process comprises separating said solid from said leachate and washing said solid so as to obtain silica having a purity of at least 98 %.

178. The process of any one of claims 132 to 175, wherein said process comprises separating said solid from said leachate and washing said solid so as to obtain silica having a purity of at least 99 %.

179. The process of any one of claims 132 to 178, wherein said process comprises reacting said leachate with gaseous HCl so as to obtain said liquid and said precipitate comprising said aluminum ions, said precipitate being formed by crystallization of $AlCl_3{\bullet}6H_2O$.

180. The process of any one of claims 132 to 178, wherein said process comprises reacting said leachate with dry gaseous HCl so as to obtain said liquid and said precipitate comprising said aluminum ions, said precipitate being formed by crystallization of $AlCl_3{\bullet}6H_2O$.

181. The process of claim 179 or 180, wherein said gaseous HCl has a HCl concentration of at least 85 % by weight.

182. The process of claim 179 or 180, wherein said gaseous HCl has a HCl concentration of at least 90 % by weight.

183. The process of claim 179 or 180, wherein said gaseous HCl has a HCl concentration of about 90 % by weight.

184. The process of claim 179 or 180, wherein said gaseous HCl has a concentration of about 90 % to about 95 % by weight.

185. The process of any one of claims 179 to 184, wherein during said crystallization of $AlCl_3 \bullet 6H_2O$, said liquid is maintained at a concentration of HCl of about 25 to about 35 % by weight.

186. The process of any one of claims 179 to 184, wherein during said crystallization of $AlCl_3 \bullet 6H_2O$, said liquid is maintained at a concentration of HCl of about 30 to about 32 % by weight.

187. The process of any one of claims 179 to 184, wherein said HCl is obtained from said gaseous HCl so-produced.

188. The process of any one of claims 132 to 187, wherein said process comprises reacting said leachate with HCl recovered during said processs and ahaving a concentration of at least 30 % as to obtain said liquid and said precipitate comprising said aluminum ions, said precipitate being formed by crystallization of $AlCl_3 \bullet 6H_2O$.

189. The process of any one of claims 179 to 188, wherein said crystallization is carried out at a temperature of about 45 to about 65 °C.

190. The process of any one of claims 179 to 188, wherein said crystallization is carried out at a temperature of about 50 to about 60 °C.

191. The process of any one of claims 132 to 190, wherein said process comprises converting $AlCl_3 \bullet 6H_2O$ into $Al_2O_3$ by carrying out a calcination of $AlCl_3 \bullet 6H_2O$.

192. The process of any one of claims 132 to 190, wherein said process comprises heating said precipitate at a temperature of at least 1200 $^{o}C$ for converting $AlCl_3 \bullet 6H_2O$ into $Al_2O_3$.

193. The process of any one of claims 132 to 190, wherein said process comprises heating said precipitate at a temperature of at least 1250 $^{o}C$ for converting $AlCl_3 \bullet 6H_2O$ into $Al_2O_3$.

194. The process of any one of claims 132 to 190, wherein said process comprises heating said precipitate at a temperature of at least 900 $^{o}C$ for converting $AlCl_3 \bullet 6H_2O$ into $Al_2O_3$.

195. The process of any one of claims 132 to 190, wherein said process comprises converting $AlCl_3 \bullet 6H_2O$ into alpha-$Al_2O_3$.

196. The process of any one of claims 132 to 190, wherein said process comprises heating said precipitate at a temperature of at least 350 $^{o}C$ for converting $AlCl_3 \bullet 6H_2O$ into $Al_2O_3$.

197. The process of any one of claims 132 to 190, wherein said process comprises heating said precipitate at a temperature of about 350 $^{o}C$ to about 500 $^{o}C$ for converting $AlCl_3 \bullet 6H_2O$ into $Al_2O_3$.

198. The process of any one of claims 132 to 190, wherein said process comprises heating said precipitate at a temperature of about 375 $^{o}C$ to about 450 $^{o}C$ for converting $AlCl_3 \bullet 6H_2O$ into $Al_2O_3$.

199. The process of any one of claims 132 to 190, wherein said process comprises heating said precipitate at a temperature of about 375 $^{o}C$ to about 425 $^{o}C$ for converting $AlCl_3 \bullet 6H_2O$ into $Al_2O_3$.

200. The process of any one of claims 132 to 190, wherein said process comprises heating said precipitate at a temperature of about 385 °C to about 400 °C for converting $AlCl_3{\bullet}6H_2O$ into $Al_2O_3$.

201. The process of any one of claims 196 to 200, wherein said process comprises converting $AlCl_3{\bullet}6H_2O$ into beta-$Al_2O_3$.

202. The process of any one of claims 132 to 201, wherein converting $AlCl_3{\bullet}6H_2O$ into $Al_2O_3$ comprises carrying out a calcination via a two-stage circulating fluid bed reactor.

203. The process of any one of claims 132 to 202, wherein converting $AlCl_3{\bullet}6H_2O$ into $Al_2O_3$ comprises carrying out a calcination via a two-stage circulating fluid bed reactor that comprises a preheating system.

204. The process of claim 203, wherein said preheating system comprises a plasma torch.

205. The process of claim 203, wherein said plasma torch is effective for preheating air entering into a calcination reactor.

206. The process of claim 203, wherein said plasma torch is effective for generating steam that is injected into a calcination reactor.

207. The process of claim 203, wherein said plasma torch is effective for generating steam that is as fluidization medium in a fluid bed reactor.

208. The process of process of any one of claims 132 to 207, wherein converting $AlCl_3{\bullet}6H_2O$ into $Al_2O_3$ comprises carrying out a one-step calcination.

209. The process of process of any one of claims 132 to 208, wherein said process comprises converting $AlCl_3•6H_2O$ into $Al_2O_3$ by carrying out a calcination of $AlCl_3•6H_2O$, said calcination comprising steam injection.

210. The process of claim 209, wherein steam is injected at a pressure of about 200 to about 700 psig.

211. The process of claim 209, wherein steam is injected at a pressure of about 300 to about 700 psig.

212. The process of claim 209, wherein steam is injected at a pressure of about 400 to about 700 psig.

213. The process of claim 209, wherein steam is injected at a pressure of about 550 to about 650 psig.

214. The process of claim 209, wherein steam is injected at a pressure of about 575 to about 625 psig.

215. The process of claim 209, wherein steam is injected at a pressure of about 590 to about 610 psig.

216. The process of any one of claims 209 to 215, wherein steam is injected and a plasma torch is used for carrying fluidization.

217. The process of any one of claims 209 to 215, wherein steam is injected and a plasma torch is used for carrying fluidization.

218. The process of any one of claims 209 to 215, wherein said steam is overheated.

219. The process of any one of claims 132 to 218, wherein said process comprises converting $AlCl_3•6H_2O$ into $Al_2O_3$ by carrying out a

calcination of $AlCl_3 \bullet 6H_2O$ in which is provided by the combustion of a fossil fuel, carbon monoxide, propane, natural gas, a Refinery Fuel Gas, coal, or chlorinated gases and/or solvants.

220. The process of any one of claims 132 to 218, wherein said process comprises converting $AlCl_3 \bullet 6H_2O$ into $Al_2O_3$ by carrying out a calcination of $AlCl_3 \bullet 6H_2O$ that is provided by the combustion of gas mixture that is a an incoming smelter gas or a reducer offgas.

221. The process of any one of claims 132 to 218, wherein said process comprises converting $AlCl_3 \bullet 6H_2O$ into $Al_2O_3$ by carrying out a calcination of $AlCl_3 \bullet 6H_2O$ that is provided by the combustion of gas mixture that comprises :

$CH_4$ : 0 to about 1% vol;

$C_2H_6$ : 0 to about 2% vol;

$C_3H_8$ : 0 to about 2% vol;

$C_4H_{10}$ : 0 to about 1% vol;

$N_2$ : 0 to about 0.5% vol;

$H_2$ : about 0.25 to about 15.1 % vol;

CO : about 70 to about 82.5 % vol; and

$CO_2$ : about 1.0 to about 3.5% vol.

222. The process of claim 221, wherein $O_2$ is substantially absent from said mixture.

223. The process of any one of claims 132 to 218, wherein said process comprises converting $AlCl_3 \bullet 6H_2O$ into $Al_2O_3$ by carrying out a calcination of $AlCl_3 \bullet 6H_2O$ in which is provided by electric heating, gas heating, microwave heating.

224. The process of any one of claims 132 to 223, wherein converting $AlCl_3•6H_2O$ into $Al_2O_3$ comprises carrying out a calcination by means of fluid bed reactor.

225. The process of claim 224, wherein the fluid bed reactor comprises a metal catalyst chosen from metal chlorides.

226. The process of claim 224, wherein the fluid bed reactor comprises $FeCl_3$, $FeCl_2$ or a mixture thereof.

227. The process of claim 224, wherein the fluid bed reactor comprises $FeCl_3$.

228. The process of any one of claims 132 to 227, wherein said process is a semi-continuous process.

229. The process of any one of claims 132 to 227, wherein said process is a continuous process.

230. The process of any one of claims 132 to 229, wherein said process is effective for providing an $Al_2O_3$ recovery yield of at least 93 %.

231. The process of any one of claims 132 to 229, wherein said process is effective for providing an $Al_2O_3$ recovery yield of about 90 % to about 95 %.

232. The process of any one of claims 132 to 231, wherein said process is effective for providing a $Fe_2O_3$ recovery yield of at least 98 %.

233. The process of any one of claims 132 to 231, wherein said process is effective for providing a $Fe_2O_3$ recovery yield of about 98 % to about 99.5 %.

234. The process of any one of claims 132 to 233, wherein said process is effective for providing a MgO recovery yield of at least 96 %.

235. The process of any one of claims 132 to 233, wherein said process is effective for providing a MgO recovery yield of about 96 to about 98 %.

236. The process of any one of claims 132 to 235, wherein said process is effective for providing a HCl recovery yield of at least 98 %.

237. The process of any one of claims 132 to 235, wherein said process is effective for providing a HCl recovery yield of at least 99 %.

238. The process of any one of claims 132 to 235, wherein said process is effective for providing a HCl recovery yield of about 98 to about 99.9 %.

239. The process of any one of claims 132 to 238, wherein said aluminum-containing material is leached at a pressure of about 4 to about 10 barg.

240. The process of any one of claims 132 to 238, wherein said aluminum-containing material is leached at a pressure of about 4 to about 8 barg.

241. The process of any one of claims 132 to 238, wherein said aluminum-containing material is leached at a pressure of about 5 to about 6 barg.

242. The process of any one of claims 132 to 241, further comprising, before leaching said aluminum-containing material, a pre-leaching removal of fluorine optionally contained in said aluminum-containing material.

243. The process of any one of claims 132 to 242, comprising leaching said aluminum-containing material with HCl so as to obtain said leachate comprising aluminum ions and said solid, separating said solid from said leachate; and further treating said solid so as to separate $SiO_2$ from $TiO_2$ that are contained therein.

244. The process of any one of claims 132 to 242, comprising leaching said aluminum-containing material with HCl so as to obtain said leachate comprising aluminum ions and said solid, separating said solid from said leachate; and further treating said solid with HCl so as to separate $SiO_2$ from $TiO_2$ that are contained therein.

245. The process of any one of claims 132 to 244, comprising leaching said aluminum-containing material with HCl so as to obtain said leachate comprising aluminum ions and said solid, separating said solid from said leachate; and further treating said solid with HCl at a concentration of less than 20 % by weight, at a temperature of less than 85 °C, in the presence of MgCl, so as to separate $SiO_2$ from $TiO_2$ that are contained therein.

246. The process of any one of claims 132 to 245, wherein said aluminum-5containing material is chosen from aluminosilicate minerals.

247. The process of any one of claims 132 to 245, wherein said aluminum-containing material is argillite.

248. The process of any one of claims 132 to 245, wherein said aluminum-containing material is bauxite.

249. The process of any one of claims 132 to 245, wherein said aluminum-containing material is an industrial refractory material.

250. The process of any one of claims 132 to 245, wherein said aluminum-containing material is red mud.

251. The process of any one of claims 132 to 250, wherein said process is effective for avoiding producing red mud.

252. The process of any one of claims 132 to 251, wherein the recovered HCl is purified and/or concentrated.

253. The process of claim 252, wherein the recovered HCl is purified by means of a membrane distillation process.

254. The process of claim 252, wherein the recovered HCl is gaseous HCl and is treated with $H_2SO_4$ so as to reduce the amount of water present in the gaseous HCl.

255. The process of claim 254, wherein the recovered HCl is gaseous HCl and is passed through a packed column so as to be in contact with a $H_2SO_4$ countercurrent flow so as to reduce the amount of water present in the gaseous HCl.

256. The process of claim 255, wherein the column is packed with polypropylene or polytrimethylene terephthalate.

257. The process of any one of claims 252 to 256, wherein the concentration of gaseous HCl is increased by at least 50 %.

258. The process of any one of claims 252 to 256, wherein the concentration of gaseous HCl is increased by at least 60 %.

259. The process of any one of claims 252 to 256, wherein the concentration of gaseous HCl is increased by at least 70 %.

260. The process of claim 252, wherein the recovered HCl is gaseous HCl and is treated with $CaCl_2$ so as to reduce the amount of water present in the gaseous HCl.

261. The process of claim 252, wherein the recovered HCl is gaseous HCl and is passed through a column packed with $CaCl_2$ so as to reduce the amount of water present in the gaseous HCl.

262. The process of any one of claims 252 to 261, wherein the concentration of gaseous HCl is increased from a value below the azeotropic point before treatment to a value above the azeotropic point after treatment.

263. The process of any one of claims 132 to 262, wherein said conversion of $Al_2O_3$ into aluminum is carried out by means of the Hall-Héroult process.

264. The process of any one of claims 132 to 262, wherein said conversion of $Al_2O_3$ into aluminum is carried out by using a reduction environment and carbon at temperature below 200°C.

265. The process of any one of claims 132 to 264, wherein said conversion of $Al_2O_3$ into aluminum is carried out by means of the Wohler Process.

266. The process of any one of claims 132 to 264, wherein said conversion of $Al_2O_3$ into aluminum is carried out by converting $Al_2O_3$ into $Al_2S_3$ and then converting $Al_2S_3$ into aluminum.

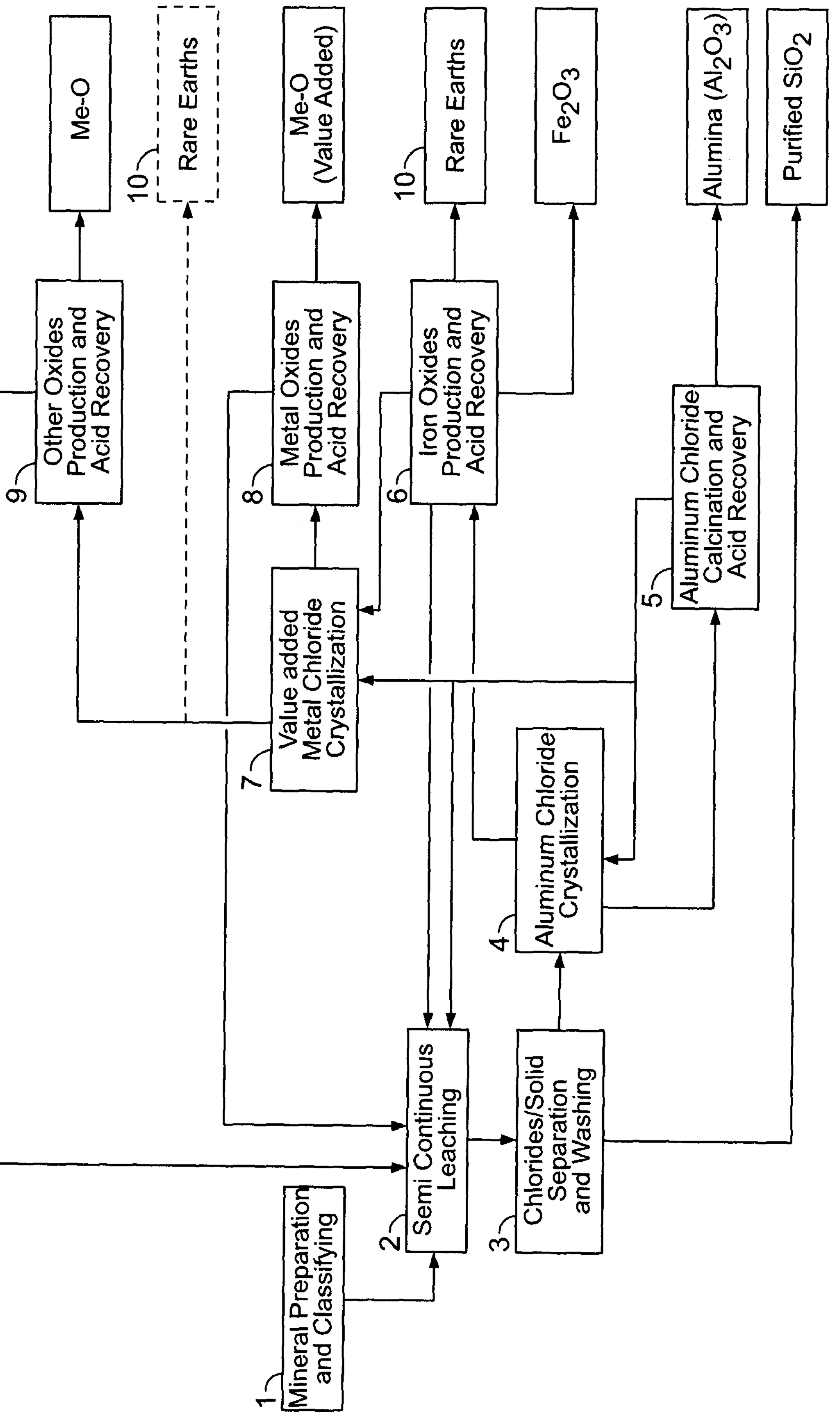
1 Mineral Preparation and Classifying
2 Semi Continuous Leaching
3 Chlorides/Solid Separation and Washing
4 Aluminum Chloride Crystallization
5 Aluminum Chloride Calcination and Acid Recovery
6 Iron Oxides Production and Acid Recovery
7 Value added Metal Chloride Crystallization
8 Metal Oxides Production and Acid Recovery
9 Other Oxides Production and Acid Recovery
10 Rare Earths
10 Rare Earths
Me-O
Me-O (Value Added)
$Fe_2O_3$
Alumina ($Al_2O_3$)
Purified $SiO_2$

FIG. 1

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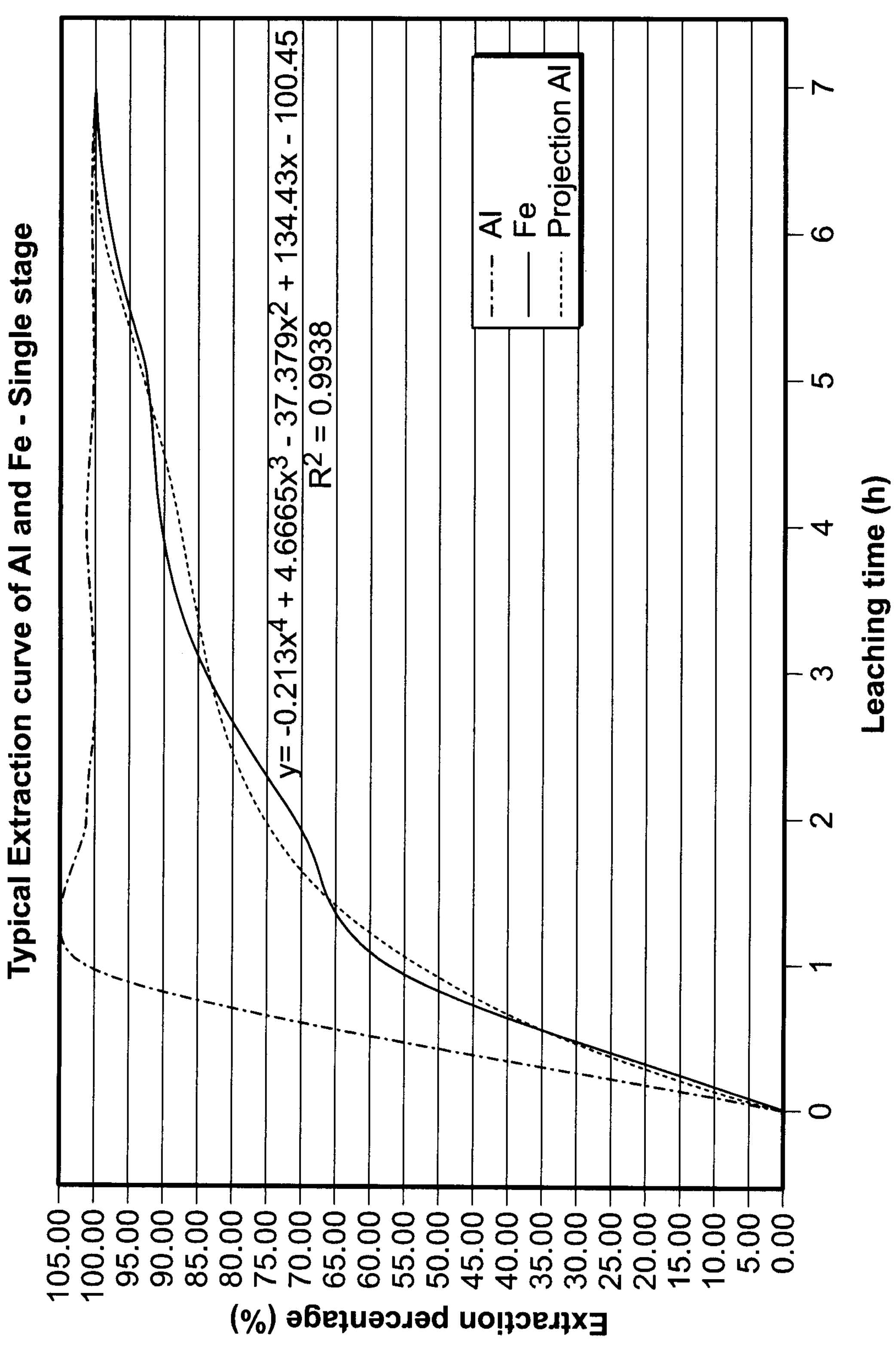

Typical Extraction curve of Al and Fe - Single stage
y= -0.213x4 + 4.6665x3 - 37.379x2 + 134.43x - 100.45
R2 = 0.9938
Al
Fe
Projection Al
Extraction percentage (%)
105.00
100.00
95.00
90.00
85.00
80.00
75.00
70.00
65.00
60.00
55.00
50.00
45.00
40.00
35.00
30.00
25.00
20.00
15.00
10.00
5.00
0.00
0
1
2
3
4
5
6
7
Leaching time (h)

FIG. 2

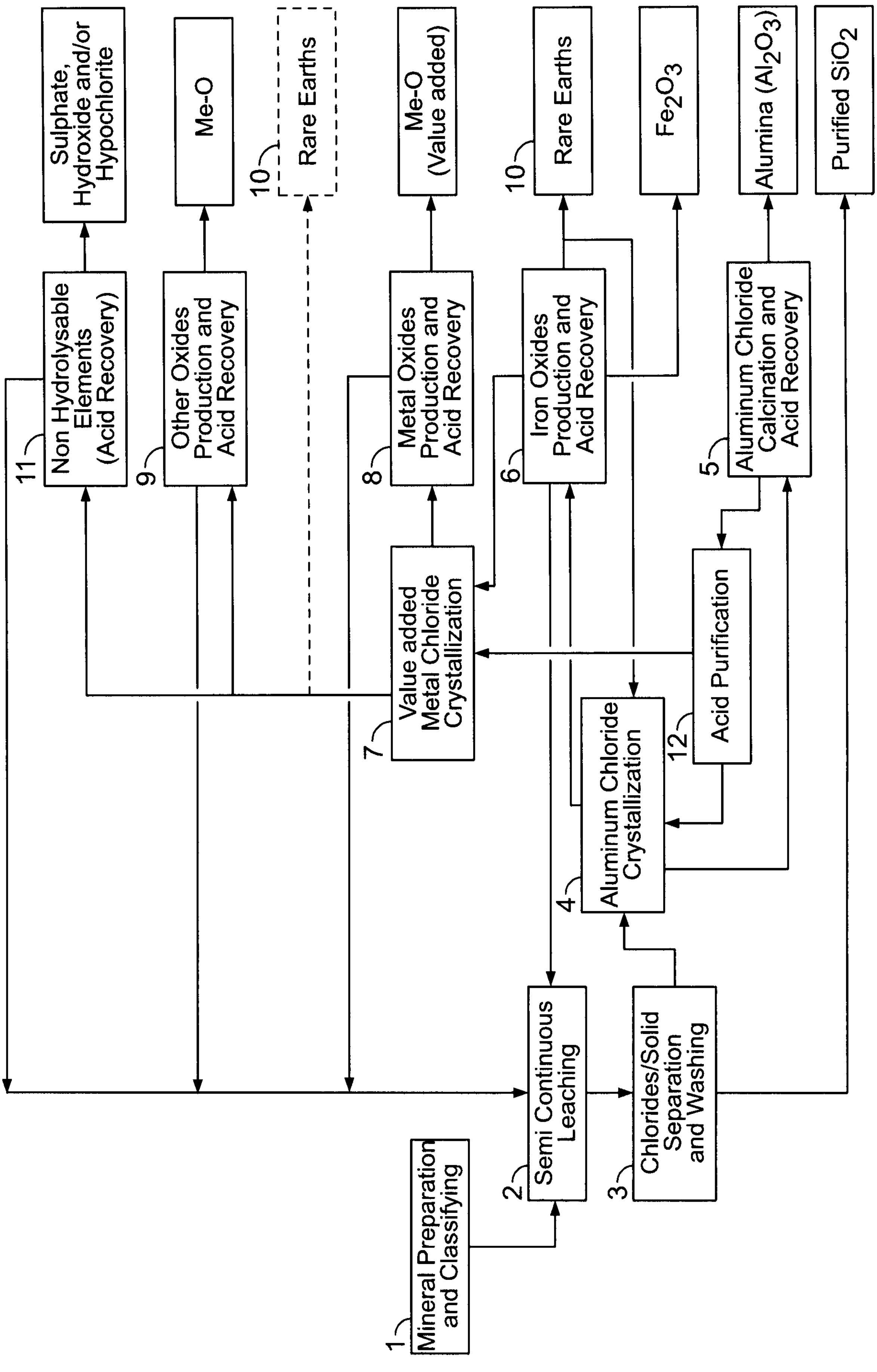

1 Mineral Preparation and Classifying
2 Semi Continuous Leaching
3 Chlorides/Solid Separation and Washing
4 Aluminum Chloride Crystallization
5 Aluminum Chloride Calcination and Acid Recovery
6 Iron Oxides Production and Acid Recovery
7 Value added Metal Chloride Crystallization
8 Metal Oxides Production and Acid Recovery
9 Other Oxides Production and Acid Recovery
10 Rare Earths
11 Non Hydrolysable Elements (Acid Recovery)
12 Acid Purification
Sulphate, Hydroxide and/or Hypochlorite
Me-O
Me-O (Value added)
Fe2O3
Alumina (Al2O3)
Purified SiO2

FIG. 3

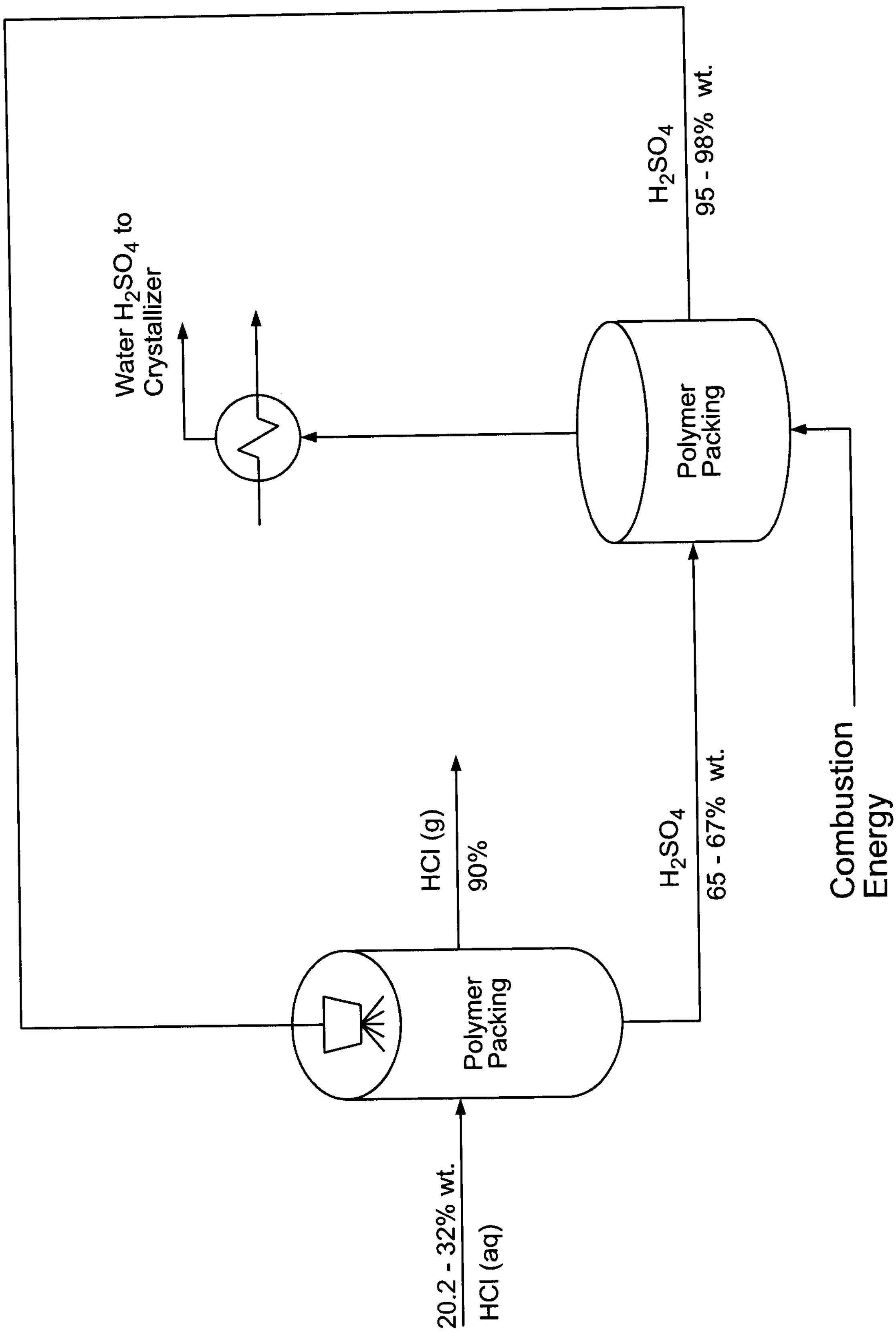
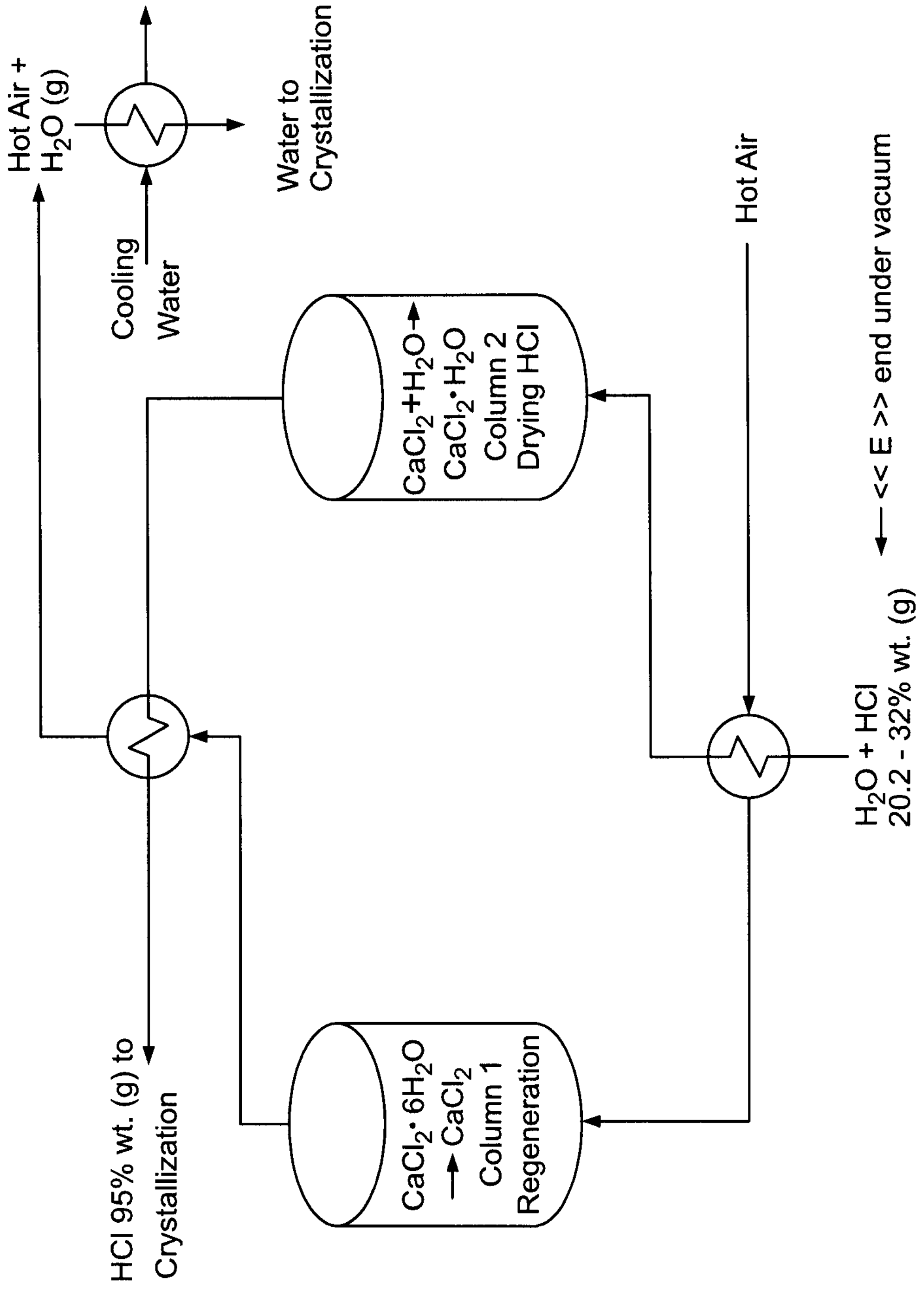

HCl (aq)
20.2 - 32% wt.
Polymer Packing
HCl (g)
90%
$H_2SO_4$
65 - 67% wt.
Combustion Energy
Polymer Packing
Water $H_2SO_4$ to Crystallizer
$H_2SO_4$
95 - 98% wt.

FIG. 4



Hot Air + $H_2O$ (g)
Cooling Water
Water to Crystallization
$CaCl_2 + H_2O \rightarrow CaCl_2 \cdot H_2O$
Column 2
Drying HCl
Hot Air
<< E >> end under vacuum
$H_2O$ + HCl
20.2 - 32% wt. (g)
HCl 95% wt. (g) to Crystallization
$CaCl_2 \cdot 6H_2O \rightarrow CaCl_2$
Column 1
Regeneration


**FIG. 5**

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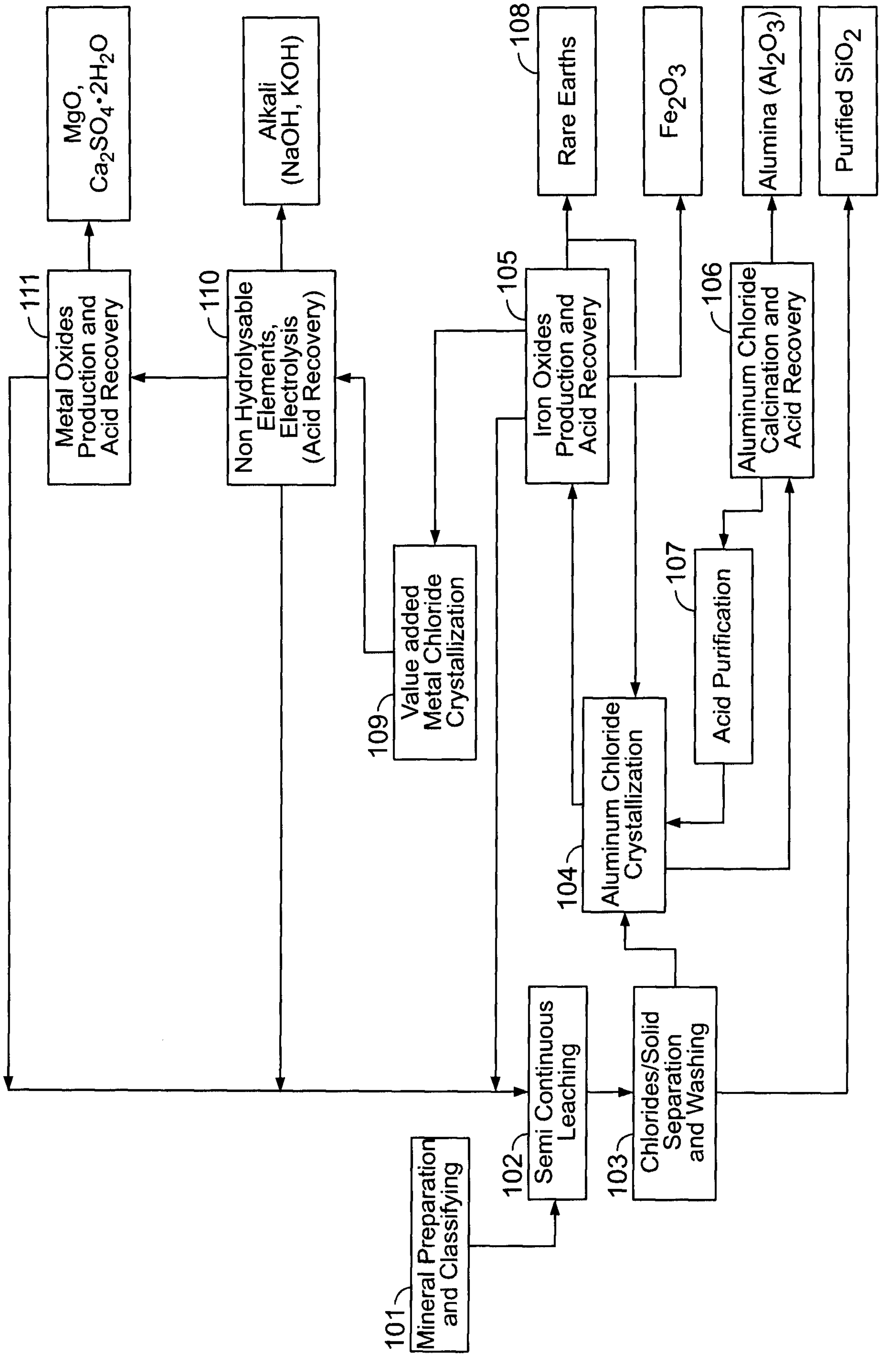
101 Mineral Preparation and Classifying
102 Semi Continuous Leaching
103 Chlorides/Solid Separation and Washing
104 Aluminum Chloride Crystallization
105 Iron Oxides Production and Acid Recovery
106 Aluminum Chloride Calcination and Acid Recovery
107 Acid Purification
108 Rare Earths
109 Value added Metal Chloride Crystallization
110 Non Hydrolysable Elements, Electrolysis (Acid Recovery)
111 Metal Oxides Production and Acid Recovery
MgO, $Ca_2SO_4 \cdot 2H_2O$
Alkali (NaOH, KOH)
$Fe_2O_3$
Alumina ($Al_2O_3$)
Purified $SiO_2$

FIG. 6

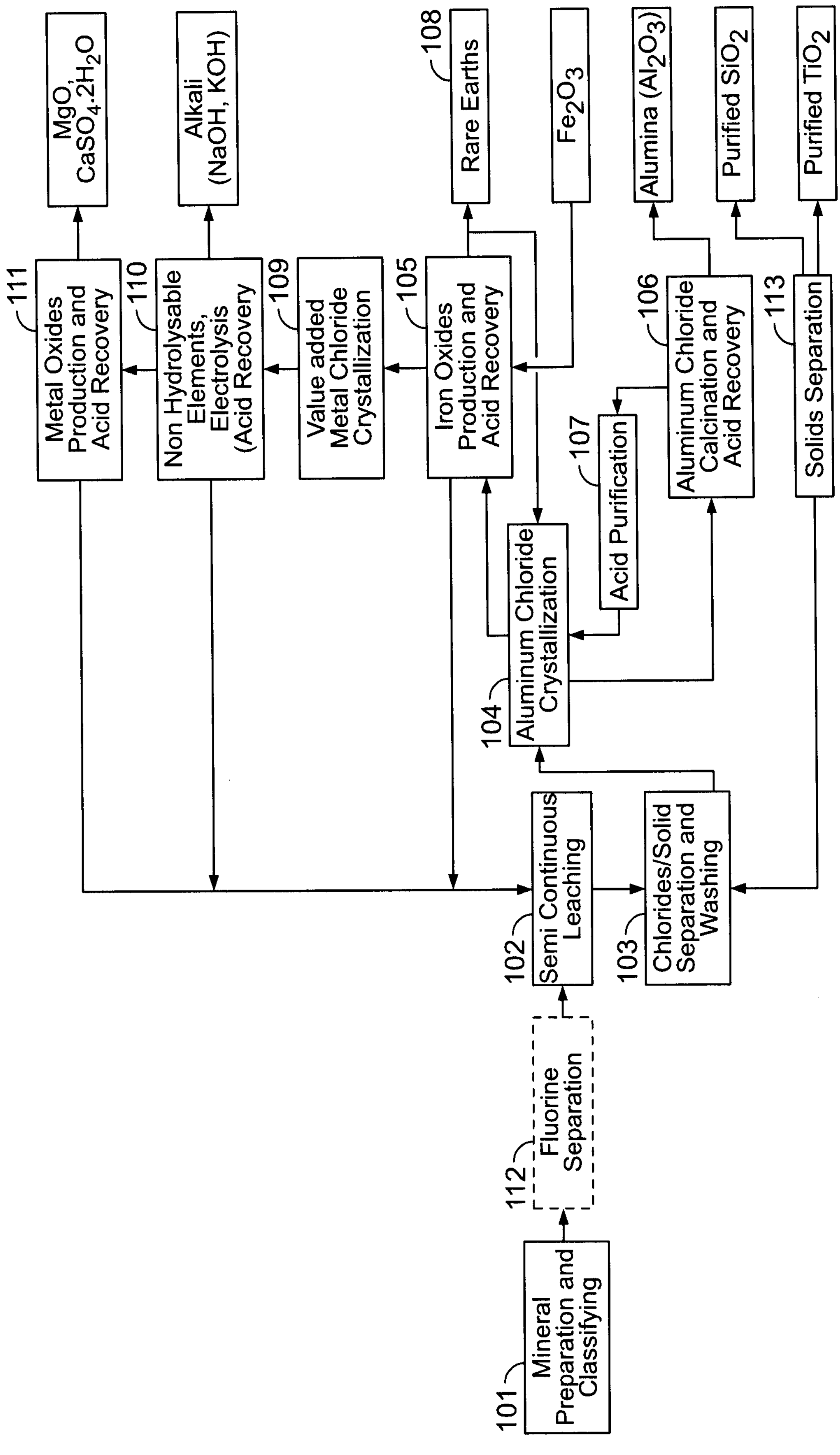
101
Mineral Preparation and Classifying
112
Fluorine Separation
102
Semi Continuous Leaching
103
Chlorides/Solid Separation and Washing
104
Aluminum Chloride Crystallization
107
Acid Purification
106
Aluminum Chloride Calcination and Acid Recovery
113
Solids Separation
105
Iron Oxides Production and Acid Recovery
109
Value added Metal Chloride Crystallization
110
Non Hydrolysable Elements, Electrolysis (Acid Recovery
111
Metal Oxides Production and Acid Recovery
MgO, CaSO4.2H2O
Alkali (NaOH, KOH)
108
Rare Earths
Fe2O3
Alumina (Al2O3)
Purified SiO2
Purified TiO2

FIG. 7

| **INTERNATIONAL SEARCH REPORT** | International application No. PCT/CA2012/000871 |
|---|---|

A. CLASSIFICATION OF SUBJECT MATTER

IPC: ***C01F 7/30*** (2006.01) , ***C01F 7/02*** (2006.01) , ***C01F 7/56*** (2006.01) , ***C22B 3/10*** (2006.01) , ***C22B 3/46*** (2006.01) , ***C22B 21/00*** (2006.01)

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC: ***C01F 7/30*** (2006.01) , ***C01F 7/02*** (2006.01) , ***C01F 7/56*** (2006.01) , ***C22B 3/10*** (2006.01) , ***C22B 3/46*** (2006.01) , ***C22B 21/00*** (2006.01)

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

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

Databases: Canadian Patent Database (CPD); TotalPatent; EPODOC

Search Terms: alumina or $Al_2O_3$ or (alumin?um oxide), HCl or hydrochloric, leach*, heat* or calcin*, $AlCl_3$ or (alumin?um chloride)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X<br>-<br>Y | US 4,222,989 A (BELSKY et al.) 16 September 1980 (16-09-1980)<br>*see abstract; col. 2, lines 46-49, 60-68; col. 3, lines 9, 17-18, 29-31, 40-41, 45-65; col. 4, lines 5, 65-66; col. 5, lines 55-64; col. 6, lines 1-3, 15-24; col. 7, lines 35-38; Figure 1 and Example I | 1-26, 29, 45-157, 160, 176-266<br>-<br>27-44, 132-266 |
| X<br>-<br>Y | CA 2 240 067 A1 (NEHARI et al.) 26 June 1997 (26-06-1997)<br>**see claim 1; page 3, line 25 - page 6, line ; page 4, lines 13-15; page 5, lines 8-10, 31;page 6, lines 8-17; Figure 1; Examples 1-3 | 1-26, 29, 45-157, 160, 176-266<br>-<br>27-44, 132-266 |
| X<br>-<br>Y | CA 2 610 918 A1 (BEAULIEU et al.) 22 February 2008 (22-02-2008)<br>**see abstract; claims 1-10, 14-17, 20, 26, 28, 31; page 1, last paragraph; Example | 1-26, 29, 45-157, 160, 176-266<br>-<br>27-44, 132-266 |
| X<br>-<br>Y | CA 1 066 872 A1 (MESSNER) 27 November 1979 (27-11-1979)<br>**see entire document | 1-26, 29, 45-157, 160, 176-266<br>-<br>27-44, 132-266 |

[X] Further documents are listed in the continuation of Box C. [X] 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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"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 |
|---|---|
| 6 December 2012 (06-12-2012) | 11 January 2013 (11-01-2013) |


| Name and mailing address of the ISA/CA | Authorized officer |
|---|---|
| Canadian Intellectual Property Office<br>Place du Portage I, C114 - 1st Floor, Box PCT<br>50 Victoria Street<br>Gatineau, Quebec K1A 0C9<br>Facsimile No.: 001-819-953-2476 | Heather Hurley (819) 994-0472 |

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| D, Y | WO2009/153321 A1 (TAKAHASHI et al.) 23 December 2009 (23-12-2009)<br>**see page 1, paragraphs 1 and 3; and claim 1 | 27-44, 158-175 |
| D, Y | US 5,876,584 A (CORTELLINI) 2 March 1999 (02-03-1999)<br>**see abstract | 132-266 |
| D, Y | US 6,565,733 B1 (SPORTEL et al.) 20 May 2003 (20-05-2003)<br>**see abstract | 132-266 |
| D, E | WO2012/126092 A1 (BOUDREAULT et al.) 27 September 2012 (27-09-2012)<br>**see entire document | 1-266 |
| D, E | WO2012/149642 A1 (BOUDREAULT et al.) 8 November 2012 (08-11-2012)<br>**see entire document | 1-266 |

| Patent Document Cited in Search Report | Publication Date | Patent Family Member(s) | Publication Date |
|---|---|---|---|
| US4222989A | 16 September 1980 (16-09-1980) | CA1154233A1 | 27 September 1983 (27-09-1983) |
| | | DE2803483A1 | 2 August 1979 (02-08-1979) |
| | | DE2803483C2 | 5 August 1982 (05-08-1982) |
| | | GB2013164A | 8 August 1979 (08-08-1979) |
| | | GB2013164B | 21 July 1982 (21-07-1982) |
| CA2240067A1 | 26 June 1997 (26-06-1997) | AT182128T | 15 July 1999 (15-07-1999) |
| | | AU713938B2 | 16 December 1999 (16-12-1999) |
| | | AU7707996A | 14 July 1997 (14-07-1997) |
| | | BR9612010A | 28 December 1999 (28-12-1999) |
| | | CN1207719A | 10 February 1999 (10-02-1999) |
| | | CN1085622C | 29 May 2002 (29-05-2002) |
| | | CZ9801849A3 | 17 March 1999 (17-03-1999) |
| | | DE69603289D1 | 19 August 1999 (19-08-1999) |
| | | DE69603289T2 | 09 December 1999 (09-12-1999) |
| | | EP0866769A1 | 30 September 1998 (30-09-1998) |
| | | EP0866769B1 | 14 July 1999 (14-07-1999) |
| | | ES2134649T3 | 01 October 1999 (01-10-1999) |
| | | HK1014923A1 | 20 April 2000 (20-04-2000) |
| | | HU0001163A2 | 28 August 2000 (28-08-2000) |
| | | HU0001163A3 | 30 July 2001 (30-07-2001) |
| | | IL116409D0 | 31 March 1996 (31-03-1996) |
| | | IL116409A | 30 November 1999 (30-11-1999) |
| | | JP2000505034A | 25 April 2000 (25-04-2000) |
| | | RU2176984C2 | 20 December 2001 (20-12-2001) |
| | | US5993758A | 30 November 1999 (30-11-1999) |
| | | WO9722554A1 | 26 June 1997 (26-06-1997) |
| | | ZA9610486A | 24 June 1997 (24-06-1997) |
| CA2610918A1 | 22 February 2008 (22-02-2008) | CA2610918A1 | 22 February 2008 (22-02-2008) |
| | | CA2610918C | 10 March 2009 (10-03-2009) |
| | | US2008159935A1 | 03 July 2008 (03-07-2008) |
| | | US7651676B2 | 26 January 2010 (26-01-2010) |
| CA1066872A1 | 27 November 1979 (27-11-1979) | None | |
| WO2009153321A1 | 23 December 2009 (23-12-2009) | AU2009259366A1 | 23 December 2009 (23-12-2009) |
| | | CA2728504A1 | 23 December 2009 (23-12-2009) |
| | | CN102066262A | 18 May 2011 (18-05-2011) |
| | | EP2310323A1 | 20 April 2011 (20-04-2011) |
| | | EP2310323B1 | 06 June 2012 (06-06-2012) |
| | | ES2391743T3 | 29 November 2012 (29-11-2012) |
| | | JP2010024136A | 04 February 2010 (04-02-2010) |
| | | MX2010013443A | 21 April 2011 (21-04-2011) |
| | | RU2011101736A | 27 July 2012 (27-07-2012) |
| | | US2011158869A1 | 30 June 2011 (30-06-2011) |
| US5876584A | 02 March 1999 (02-03-1999) | AT178105T | 15 April 1999 (15-04-1999) |
| | | AU698926B2 | 12 November 1998 (12-11-1998) |
| | | AU5874096A | 11 December 1996 (11-12-1996) |
| | | BR9608828A | 15 June 1999 (15-06-1999) |
| | | CA2219890A1 | 28 November 1996 (28-11-1996) |
| | | CA2219890C | 14 August 2001 (14-08-2001) |
| | | CN1185815A | 24 June 1998 (24-06-1998) |
| | | CN1078267C | 23 January 2002 (23-01-2002) |
| | | DE69601870D1 | 29 April 1999 (29-04-1999) |
| | | DE69601870T2 | 26 August 1999 (26-08-1999) |
| | | EP0828866A1 | 18 March 1998 (18-03-1998) |
| | | EP0828866B1 | 24 March 1999 (24-03-1999) |
| | | NO975404A | 25 November 1997 (25-11-1997) |
| | | NO975404D0 | 25 November 1997 (25-11-1997) |
| Continued on Extra Sheet | | | |
| US6565733B1 | 20 May 2003 (20-05-2003) | AT305985T | 15 October 2005 (15-10-2005) |
| | | AU761852B2 | 12 June 2003 (12-06-2003) |

| Patent Document Cited in Search Report | Publication Date | Patent Family Member(s) | Publication Date |
|---|---|---|---|
| US5876584A (CONTINUED) | 02 March 1999 (02-03-1999) | NO318238B1 | 21 February 2005 (21-02-2005) |
| | | NZ308879A | 25 November 1998 (25-11-1998) |
| | | RU2133302C1 | 20 July 1999 (20-07-1999) |
| | | US5560809A | 01 October 1996 (01-10-1996) |
| | | WO9637637A1 | 28 November 1996 (28-11-1996) |
| US6565733B1 | 20 May 2003 (20-05-2003) | AT305985T | 15 October 2005 (15-10-2005) |
| | | AU761852B2 | 12 June 2003 (12-06-2003) |
| | | AU2284500A | 12 July 2000 (12-07-2000) |
| | | CA2355662A1 | 29 June 2000 (29-06-2000) |
| | | CA2355662C | 25 July 2006 (25-07-2006) |
| | | DE19983811T1 | 28 February 2002 (28-02-2002) |
| | | DE69927605D1 | 16 February 2006 (16-02-2006) |
| | | DE69927605T2 | 03 August 2006 (03-08-2006) |
| | | EP1141425A1 | 10 October 2001 (10-10-2001) |
| | | EP1141425B1 | 05 October 2005 (05-10-2005) |
| | | ES2251257T3 | 16 April 2006 (16-04-2006) |
| | | JP2003528976A | 30 September 2003 (30-09-2003) |
| | | JP4416953B2 | 17 February 2010 (17-02-2010) |
| | | NO20013011D0 | 18 June 2001 (18-06-2001) |
| | | NO20013011A | 17 August 2001 (17-08-2001) |
| | | NO331582B1 | 30 January 2012 (30-01-2012) |
| | | RU2233897C2 | 10 August 2004 (10-08-2004) |
| | | WO0037691A1 | 29 June 2000 (29-06-2000) |
| WO2012126092A1 | 27 September 2012 (27-09-2012) | WO2012149642A1 | 08 November 2012 (08-11-2012) |
| WO2012149642A1 | 08 November 2012 (08-11-2012) | WO2012126092A1 | 27 September 2012 (27-09-2012) |