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(40) Title: PROCESSES FOR EXTRACTING ALUMINUM AND IRON FROM ALUMINOUS ORES
(54) Title: PROCESSES FOR EXTRACTING ALUMINUM AND IRON FROM ALUMINOUS ORES
(57) Abstract: There are provided processes and compositions for extracting aluminum and/or iron ions from aluminous ores or a mixture. One process comprises recovering said aluminum ions from a composition comprising said aluminum ions, said iron ions, an organic solvent and an extracting agent adapted to form an organometallic complex substantially selectively with said iron ions or with said aluminum ions which is soluble in said organic solvent. Another process for extracting aluminum from an ore comprising leaching said ore with an acid so as to obtain a leachate and a solid residue and removing at least a portion of iron ions contained in said leachate by either substantially selectively precipitating said at least a portion of said iron ions in basic conditions in which the pH is of at least 10, or substantially selectively complexing said at least a portion of said iron ions with an extracting agent adapted to form an organometallic complex. Another process for at least partially separating aluminum ions from iron ions comprised in a composition comprises substantially selectively precipitating at least a portion of said iron ions in basic conditions in which the pH is at least 10.
(60) Fig. 1
GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, Published:
ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI,
FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL,
NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG,
CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
TECHNICAL FIELD

[0001] The present invention relates to improvements in the field of chemistry applied to extraction of aluminum from aluminous ores. For example, such processes are useful for extracting aluminum from aluminous ores comprising various types of metals such as Fe, K, Mg, Na, Ca, Mn, Ba, Zn, Li, Sr, V, Ni, Cr, Pb, Cu, Co, Sb, As, B, Sn, Be, Mo, or mixtures thereof.

BACKGROUND OF THE INVENTION

[0002] More than 96 % of the alumina which is produced worldwide is obtained from bauxite, which is a mineral that is particularly rich in alumina (40 - 60 %) and whose main suppliers are from Jamaica, Australia, Brazil, Africa and Russia. In certain areas of the world there are large quantities of aluminous ores, which are aluminosilicates (for example argillite, nepheline, etc.) that are relatively rich in alumina (20 - 28 %). However such areas have received little attention up to now because the production costs for extracting aluminum from such ores remained too high. In these aluminous materials, and contrary to bauxite, aluminum oxide is associated with silicated or sulfated phases. Thus, the Bayer process cannot be used, which means that alternative treatments for the production of alumina must be used or developed. Various processes have been proposed so far in order to extract aluminum from such aluminous ores comprising aluminosilicates but there is still room for improvement or for alternative routes.

SUMMARY OF THE INVENTION

[0003] According to one aspect, there is provided a process for extracting aluminum ions from a mixture comprising iron ions and the aluminum ions. The process comprises recovering the aluminum ions from a composition comprising the aluminum ions, the iron ions, an organic solvent and an extracting agent adapted to form an organometallic complex substantially
selectively with the iron ions or with the aluminum ions which is soluble in the organic solvent.

[0004] According to one embodiment, the composition can comprise an acidic aqueous phase comprising aluminum ions and an organic phase comprising iron ions complexed with the extracting agent and wherein the aluminum ions are recovered by separating the aqueous phase from the organic phase. The aqueous phase can have a pH of about 1 to about 2.5 or of about 2. The extracting agent can be chosen from phosphoric acids and derivatives thereof, and phosphinic acids and derivatives thereof. For example, the extracting agent can be chosen from di-2-ethylhexyl phosphoric acid (HDEHP), bis(2,4,4-trimethylpentyl) phosphinic acid and 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester. The extracting agent can have a concentration of about 0.5 M to about 1.5 M in the organic phase or of about 1 M in the organic phase. The composition can have a volumic ratio organic phase : aqueous phase of about 1:1. After extraction (passing the composition through the membrane), the aqueous phase can be separated from the organic phase, and the aluminum ions can recovered in the aqueous phase and the aqueous phase can be treated with a base (for example NaOH, KOH, or a mixture thereof). The aqueous phase can be treated with the base so as to obtain a pH of at least about 4. The process can further comprise treating the organic phase with HCl and isolating the iron ions in the form of Fe$^{3+}$.

[0005] According to another embodiment, the composition can comprise an acidic aqueous phase comprising iron ions and an organic phase comprising aluminum ions complexed with the extracting agent, and wherein the aluminum ions are recovered by separating the aqueous phase from the organic phase. The aqueous phase can have a pH of about 2.5 to about 3.5. The extracting agent can be a phosphinic acid or a derivative thereof. For example, the extracting agent can be bis(2,4,4-trimethylpentyl) phosphinic acid. The extracting agent can have a concentration of about 10 % to about 25 % v/v with respect to the organic solvent or of about 20 % v/v with respect to the organic solvent. The composition can have a volumic ratio aqueous phase : organic phase of about 1:1 to about 1:3. During the process, the
composition can be at a temperature of about 30 °C to about 50 °C or at a
temperature of about 35 °C to about 45 °C. After extraction through the
membrane, the aqueous phase can be separated from the organic phase.
The complexed aluminum ions can be recovered in the organic phase. The
organic phase can then be treated with HCl so as to obtain an aqueous
composition comprising the aluminum ions.

[0006] For example, the organic solvent can be chosen from
hydrocarbons. For example, the organic solvent can be chosen from C₅-C₁₂
alkanes and mixtures thereof. The organic solvent can also be hexane or
heptane. The organic phase and the aqueous phase can be separated by
means of a filtration membrane, for example a hollow fiber membrane. Such
membrane can comprise polypropylene, polyvinylidene difluoride, or a mixture
thereof. The aqueous phase can be treated with the base so as to obtain a pH
of at least about 4. The process can also further comprise a separation by
filtration so as to obtain Al(OH)₃. The process can also comprise washing the
Al(OH)₃. The process can also comprise converting Al(OH)₃ into Al₂O₃.
Conversion of Al(OH)₃ into Al₂O₃ can be carried out at a temperature of about
800 °C to about 1200 °C.

[0007] According to another aspect there is provided a composition
comprising aluminum ions, iron ions, an organic solvent and an extracting
agent adapted to form an organometallic complex substantially selectively
with the iron ions or with the aluminum ions which is soluble in the organic
solvent.

[0008] According to another aspect, there is provided a composition
comprising an acidic aqueous phase comprising aluminum ions and an
organic phase comprising iron ions complexed with an extracting agent.

[0009] According to another aspect, there is provided a composition
comprising an acidic aqueous phase comprising iron ions and an organic
phase comprising aluminum ions complexed with an extracting agent.
The various parameters, embodiments and examples previously described concerning the processes can also be applied, when possible, to these compositions.

According to another aspect, there is provided a process for at least partially separating aluminum ions from iron ions comprised in a composition, the process comprising substantially selectively precipitating at least a portion of the iron ions in basic conditions in which the pH is of at least 10. The iron ions can be precipitated from a basic aqueous composition comprising NaOH or KOH. For example, the base can be reacted with the composition so as to obtain a mixture in which the pH is of at least 10, and then, the at least portion of precipitated iron ions can be separated from the rest of the mixture. For example, the precipitated iron ions can be separated from the rest of the mixture by carrying out a filtration, a decantation, a centrifugation, or combinations thereof. The process can further comprise rinsing the obtained precipitated iron ions with a basic solution. The basic solution can have a concentration of about 0.01 M to about 0.02 M. The pH can be at least 11, at least 12, about 10.8 to about 11.2, or about 11.5 to about 12.5. The process can further comprise purifying the precipitated iron ions by means of a hollow fiber membrane.

According to another aspect, there is provided a process for extracting aluminum from an aluminum ore, the process comprising:

- leaching the aluminum ore with an acid so as to obtain a leachate and a solid residue;

- removing at least a portion of iron ions contained in the leachate by:

  (i) substantially selectively precipitating the at least portion of the iron ions in basic conditions in which the pH is of at least 10, so as to obtain an aluminum enriched composition; or
(ii) substantially selectively complexing the at least portion of the iron ions with an extracting agent adapted to form an organometallic complex substantially selectively with the iron ions so as to obtain an aluminum enriched composition.

[0013] For example, the acid can be HCl. The aluminum ore can leached with HCl at a temperature of at least 80 °C, at least 90 °C, or about 100 °C to about 110 °C. HCl can have a concentration of about 6 M. The aluminum ore / acid ratio can be about 1 / 10 in weight by volume.

[0014] For example, the removal of the at least portion of iron ions can be carried out by precipitating the iron ions from a basic aqueous composition. The composition can comprise comprising NaOH or KOH.

[0015] For example, the removal of the at least portion of iron ions can be carried out by reacting the leachate with a base in order to obtain a pH of at least 10 and precipitating the iron ions.

[0016] For example, the precipitated iron ions can be separated from the rest of the leachate by carrying out a filtration, a decantation, a centrifugation, or mixtures thereof.

[0017] The process can further comprise rinsing the obtained precipitated iron ions with a basic solution. The basic solution can have a concentration of about 0.01 M to about 0.02 M. The pH can be at least 11, at least 12, about 10.8 to about 11.2, or about 11.5 to about 12.5. The process can further comprise purifying the precipitated iron ions by means of a hollow fiber membrane.

[0018] The removal of the at least portion of iron ions can be carried out by reacting the leachate, under acidic conditions, with the extracting agent and an organic solvent in order to obtain a composition comprising an acidic aqueous phase comprising aluminum ions and an organic phase comprising iron ions complexed with the extracting agent. The aluminum enriched composition can be obtained by separating the aqueous phase from the
organic phase. The aqueous phase can have a pH of about 1 to about 2.5, or about 2. The extracting agent can be chosen from di-2-ethylhexyl phosphoric acid (HDEHP), bis(2,4,4-trimethylpentyl) phosphinic acid and 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester. The extracting agent can have a concentration of about 0.5 M to about 1.5 M in the organic phase or about 1 M in the organic phase.

[0019] For example, the organic solvent can be chosen from C5-C12 alkanes and mixtures thereof. The organic solvent can be heptane. The composition can have a volumic ratio organic phase : aqueous phase of about 1:1. The organic phase and the aqueous phase can be separated by means of a filtration membrane. The membrane can be a hollow fiber membrane. The membrane can comprise polypropylene, polyvinylidene difluoride, or a mixture thereof.

[0020] After passing the composition through the membrane, the aqueous phase can separated from the organic phase. The aluminum ions can be recovered in the aqueous phase and the aqueous phase is treated with a base (such as NaOH or KOH). The aqueous phase can be treated with the base so as to obtain a pH of at least about 4. The process can further comprise a separation by filtration to obtain Al(OHh, which can be eventually washed.

[0021] For example, the aluminum ore can be crushed and roasted before being leached.

[0022] For example, before removal of the iron ions, the leachate is treated with a base.

[0023] For example, before removal of the iron ions, the leachate can be distilled so as to reduce its volume.

[0024] For example, the process can further comprise at least partially recovering the aluminum ions present in the aluminum enriched composition.
For example, the aluminum enriched composition can be treated with an extracting agent adapted to form an organometallic complex substantially selectively with the aluminum ions in the presence of an organic solvent and an acid solution in order to form a composition comprising an acidic aqueous phase comprising impurities and an organic phase comprising aluminum ions complexed with the extracting agent. The aluminum ions can be recovered by separating the aqueous phase from the organic phase. For example, the aqueous phase can have a pH of about 2.5 to about 3.5. The extracting agent can be a phosphinic acid or a derivative thereof. The extracting agent can be bis(2,4,4-trimethylpentyl) phosphinic acid. The extracting agent can have a concentration of about 10 % to about 25 % v/v or about 20 % v/v with respect to the organic solvent. The organic solvent can be chosen from C₅-C₁₂ alkanes and mixtures thereof. The organic solvent can be heptane. The composition can have a volumic ratio aqueous phase : organic phase of about 1:1 to about 1:3. The organic phase and the aqueous phase can be separated by means of a membrane (for example a hollow fiber membrane). The membrane can comprise polypropylene, polyvinylidene difluoride, or a mixture thereof. The composition can be at a temperature of about 30 °C to about 50 °C, or about 35 °C to about 45 °C. After passing the composition through the membrane, the aqueous phase can be separated from the organic phase. The complexed aluminum ions can be recovered in the organic phase. The organic phase can then be treated with HCl so as to obtain an aqueous composition comprising the aluminum ions. The aluminum ions can be converted into Al(OH)₃ by contacting it with a base. Al(OH)₃ can then be converted into Al₂O₃. Such a conversion of Al(OH)₃ into Al₂O₃ can be carried out at a temperature of about 800 °C to about 1200 °C.

**BRIEF DESCRIPTION OF DRAWINGS**

In the following drawings, which represent by way of example only, various embodiments of the invention:

Fig. 1 shows a bloc diagram of a process according to one embodiment of a process for extracting aluminum from an aluminous ore.
DETALLED DESCRIPTION OF VARIOUS EMBODIMENTS

[0028] Further features and advantages will become more readily apparent from the following description of various embodiments as illustrated by way of examples only in the appended drawings wherein:

[0029] As it can be seen from Fig. 1, such a process can comprise various steps, and each of these steps can eventually be individually considered has being a process.

Preparation of argillite sample

[0030] Argillite can be finely crushed in order to help along during the following steps. For example, micronization can shorten the reaction time by few hours (about 2 to 3 hours). In order to remove most of the iron, a leaching step at room temperature is optionally carried out between the crushing step and the roasting step (see option 1). This operation is, for example, carried out with hydrochloric acid HCl (12 M) and an argillite / acid ratio (weight / volume) of 1:5 is used. Depending on experimental conditions (sizes of the particles, time of treatment, agitation system), about 65 % to about 93 % of the iron can then be removed. However, this leaching step can also bring in a certain percentage of the aluminum (0 - 5 %). The last step of the preparation of argillite comprises roasting the pretreated argillite. This can be accomplished at a temperature greater than 550 °C for a period of about 1 to 2 hours. For example, a heat treatment makes it possible to increase the quantity of extracted aluminum by about 30 % to about 40 % for the same period of time. In others words, the quantity of extracted aluminum is doubled. When leaching at room temperature is carried out, a phase separation before roasting can be made in order to recover the acid and reduce heating costs.

Acid leaching

[0031] Acid leaching comprises reacting the crushed and roasted argillite with a hydrochloric acid solution at elevated temperature during a given period of time. For example, the argillite / acid ratio can be of about of
1:10 (weight / volume), the HCl concentration can be of about 6 M, the temperature can be of about 100 °C to about 110 °C, and the reaction time can be of about 5 to about 7 hours. Under such conditions, more than about 90 % of the aluminum and about 100 % of the iron can be extracted in addition to impurities.

[0032] During the second half of such a treatment (for example the last 2 or 3 hours), a portion of the acid can be recovered by condensation. Once the extraction is terminated, the solid (argillite impoverished in metals) can be separated from the liquid by decantation or by filtration, after which it is washed. The residual leachate and the washing water may be completely evaporated. The corresponding residue can thereafter be washed many times with water so as to decrease acidity and to lower the quantities of sodium hydroxide (NaOH) that are required to adjust the pH during iron removal. Final volume accounts for 10 % to 20 % of initial volume. The acid recovered will can be re-utilized after having adjusted its titer either by adding gaseous HCl, or by adding concentrated HCl (12 M). After the reaction, the titer of the acid can vary from about 4 M to about 6 M depending on experimental conditions. With respect to the solid, it represents about 65 % to about 75 % of the initial mass of argillite, it can be valorized and be used again either as an ion exchange resin, or as an adsorbent.

**Removal of iron**

[0033] Removal of iron can be carried out by precipitation of the latter in basic medium for example at a pH of at least 10 or at a pH of about 11.5 to about 12.5. Such a step can be made by adding NaOH, for example at a concentration of 10 M. Other bases such as KOH can also be used. Then, all that is required is to separate the solid portion from the liquid portion by filtration, decantation or centrifugation and to rinse the solid by means of a diluted base, such as a solution of NaOH (for example NaOH at a concentration of 0.01 M to 0.02 M). Then, the solid is washed with distilled water. The liquid portion comprises aluminum and alkaline-earths A substantially complete removal of the iron and of nearly all the impurities
(other metals) can thus be achieved. Optionally, it is possible to recover iron by using a refining step by liquid-liquid extraction through a hollow fiber membrane (see option 2).

[0034] Alternatively (see option 3), removal of iron can be carried out by using an extracting agent and a hollow fiber membrane. Various extracting agents that could substantially selectively complex iron ions over aluminum ions (or aluminum ions over iron ions) could be used in such a step depending an Al / Fe ratio. For example, extraction can be carried out by using HDEHP (diethylhexylphosphoric acid) as an extracting agent adapted to complex iron ions. A concentration of about 1 M of HDEHP can be used in an organic solvent, such as heptane or any hydrocarbon solvent. Such an extraction can require relatively short contact times (few minutes). For example, the pH of the order of 2 can be used and aqueous phase / organic phase ratio can be of about 1:1. It was observed that is possible to extract from 86 % to 98 % iron under such conditions. It will be understood that in the present case, iron is trapped in the organic phase. To recover iron in an aqueous phase, a reverse extraction with hydrochloric acid (2 M or 6 M) and organic phase / acidic phase ratio of about 1:0.5 can then be carried out. In such a case, the resulting aqueous phase is rich in Fe\textsuperscript{3+} ions.

Aluminum recovery

[0035] The solution obtained from the previous step using either the precipitation or the extraction technique is relatively clean and mainly contains aluminum for example about 90 % to 95 % (without the alkaline-earths in the case of precipitation). Recovery of the latter can be carried out by liquid-liquid extraction for example by using a same hollow fiber membrane and an extracting agent that is adapted to complex at least substantially selectively aluminum over other metals or residues. For example, bis(2,4,4-trimethylpentyl) phosphinic acid (such as the one sold under the name Cyanex\textsuperscript{TM} 272) can be used as an extracting agent specific to aluminum. For example, this extracting agent can be used at a concentration of about 20 % v/v in an organic solvent such as heptane. The ratios between the aqueous
phase and the organic phase can be of about 1:1 to about 1:3. For example, the extraction temperatures can be of about 40 °C and the pH can be maintained at about 2.5 to about 3.5. It was observed that such a technique makes it possible to extract more than 70 - 90 % of the aluminum. After the aluminum has been trapped in the organic phase, it can be recovered in the form of a concentrate of Al³⁺ ions by using a back extraction. For example, the reverse extraction can be carried out at a temperature of about 40 °C with hydrochloric acid (for example at a concentration of 6 M). Under this condition, more than 90 % of aluminum can be recovered. Then, Al³⁺ can be converted into aluminum hydroxide Al(OH)₃ by addition of NaOH. Finally, Al(OH)₃ can be converted into alumina (alumina Al₂O₃) by roasting Al(OH)₃ for example at a temperature of about 800 °C to 1200 °C.

[0036] The following non-limiting examples further illustrate the invention.

Examples

Example 1

Preparation of argillite sample

[0037] Crushing of mudstone: The resulting micronization average employed for the tests ranges between 10 and 50 microns.

[0038] Roasting: Crushed mudstone was roasted at least during 1 hour at a temperature of 600 °C. Its average composition was:

\[
\begin{align*}
\text{Al}_2\text{O}_3 & \quad 21,0 \% \\
\text{Fe}_2\text{O}_3 & \quad 8,0 \% \\
\text{K}_2\text{O} & \quad 1,5 \% \\
\text{Na}_2\text{O} & \quad 0,9 \% \\
\text{TiO}_2 & \quad 0,9 \% \\
\text{CaO} & \quad 0,08 \% \\
\text{ZnO} & \quad 0,06 \% \\
\text{SiO}_2 & \quad 51,0 \%
\end{align*}
\]
Acid leaching

[0039] 500 g of argillite crushed and roasted were added to 5 liters of hydrochloric acid 6 M. The mixture was then heated at 100 °C - 110 °C during 7 hours.

[0040] After reaction, the liquid part was separated from the solid part by filtration. The solid was washed with distilled water which was added to the liquid portion. This washing makes it possible to recover part of the aluminum trapped in the solid. This solid had a dry mass of 345 ± 5 g, which corresponds to a loss of about 30 % - 32 %.

[0041] The remaining liquid part, containing aluminum, iron and a great part of the impurities initially present in mudstone, was reduced by evaporation at a temperature of 100 °C to 90 % of its initial volume. Residual volume was then 50 ml. The liquid compositions before and after evaporation were:

<table>
<thead>
<tr>
<th></th>
<th>Leaching solution</th>
<th>Evaporated leaching solution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Composition (%)</td>
<td>Composition (%)</td>
</tr>
<tr>
<td></td>
<td>[concentration (mg/L)]</td>
<td>[concentration (mg/L)]</td>
</tr>
<tr>
<td>Aluminum</td>
<td>47.63</td>
<td>47.86</td>
</tr>
<tr>
<td></td>
<td>[9 250]</td>
<td>[59 500]</td>
</tr>
<tr>
<td>Iron</td>
<td>31.54</td>
<td>31.07</td>
</tr>
<tr>
<td></td>
<td>[6 125]</td>
<td>[38 625]</td>
</tr>
<tr>
<td>Alkaline-earths</td>
<td>19.30</td>
<td>19.53</td>
</tr>
<tr>
<td>(Na, Mg, K, Ca)</td>
<td>[3 749]</td>
<td>[24 277]</td>
</tr>
<tr>
<td>Other metals</td>
<td>1.53</td>
<td>1.54</td>
</tr>
<tr>
<td></td>
<td>[297.3]</td>
<td>[1 920]</td>
</tr>
</tbody>
</table>

All the ions species seem to remain soluble.
Removal of iron

[0042] The residual volume was slightly diluted (+ 25 %) and concentrated hydroxide sodium (10 M) was added until a pH higher than 11.5 was reached. The formed precipitate was separated from the solution by standard filtration and was washed several times with NaOH diluted and hot ultra-pure water. The precipitate contained all the iron and the majority of the metal impurities. The filtrate contained in addition to ions Al³⁺ mainly alkaline-earths and some following impurities:

<table>
<thead>
<tr>
<th>Major filtrate impurities (%)</th>
<th>Iron</th>
<th>Sodium</th>
<th>Alkaline-earths (Mg, K, Ca)</th>
<th>Other metals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron</td>
<td>0.14</td>
<td>94.13</td>
<td>5.71</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Na⁺ came from soda and was also the Al(OH)₄⁻ counter-ion.

Aluminum recovery

[0043] The filtrate is adjusted at a pH of 2.5 to 3.5 by addition of HCl 6 M. The resulting solution is extracted by means of the complexing agent, Cyanex 272, at a concentration of 20 % volume / volume in an organic solvent with a volumetric ratio of 1:1. The extraction is carried out at a temperature of 40 °C in a membrane contactor with hollow fibers. In less than about 30 to 60 min, more than 85 % of aluminum is extracted. The pH adjustment is performed by a regulation loop controlling the NaOH (10 M) addition. Complexed Al³⁺ in Cyanex are then recovered by carrying out a back extraction with HCl (6 M) at 40 °C and an organic phase / acid phase volumetric ratio of 1:0.5. After the back extraction, the composition of the recovered acid phase is:
To increase the percentage of purity, the $\text{Al}^{3+}$ ions are precipitated in the form of $\text{Al(OH)}_3$ hydroxide, then washed several times with ultra-pure water. The composition of the hydroxide becomes:

<table>
<thead>
<tr>
<th>Composition (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
</tr>
<tr>
<td>Iron</td>
</tr>
<tr>
<td>Alkaline-earths</td>
</tr>
<tr>
<td>(Na, Mg, K, Ca)</td>
</tr>
<tr>
<td>Other metals</td>
</tr>
</tbody>
</table>

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</thead>
<tbody>
<tr>
<td>Aluminum</td>
</tr>
<tr>
<td>Iron</td>
</tr>
<tr>
<td>Alkaline-earths</td>
</tr>
<tr>
<td>(Na, Mg, K, Ca)</td>
</tr>
<tr>
<td>Other metals</td>
</tr>
</tbody>
</table>

Further purification can be performed by recrystallization.

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 extracting aluminum ions from a mixture comprising iron ions and the aluminum ions, said process comprising recovering said aluminum ions from a composition comprising said aluminum ions, said iron ions, an organic solvent and an extracting agent adapted to form an organometallic complex substantially selectively with said iron ions or with said aluminum ions which is soluble in said organic solvent.

2. The process of claim 1, wherein said composition comprises an acidic aqueous phase comprising aluminum ions and an organic phase comprising iron ions complexed with said extracting agent and wherein said aluminum ions are recovered by separating said aqueous phase from said organic phase.

3. The process of claim 2, wherein said aqueous phase has a pH of about 1 to about 2.5.

4. The process of claim 2, wherein said aqueous phase has a pH of about 2.

5. The process of any one of claims 2 to 4, wherein said extracting agent is chosen from di-2-ethylhexyl phosphoric acid (HDEHP), bis(2,4,4-trimethylpentyl) phosphinic acid and 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester).

6. The process of any one of claims 2 to 5, wherein said extracting agent has a concentration of about 0.5 M to about 1.5 M in said organic phase.

7. The process of any one of claims 2 to 5, wherein said extracting agent has a concentration of about 1 M in said organic phase.
8. The process of any one of claims 2 to 7, wherein said organic solvent is chosen from C₅-C₁₂ alkanes and mixtures thereof.

9. The process of any one of claims 2 to 7, wherein said organic solvent is heptane.

10. The process of any one of claims 2 to 9, wherein said composition has a volumic ratio organic phase : aqueous phase of about 1:1.

11. The process of any one of claims 2 to 10, wherein said organic phase and said aqueous phase are separated by means of a filtration membrane.

12. The process of claim 11, wherein said membrane is a hollow fiber membrane.

13. The process of claim 11, wherein said membrane comprises polypropylene, polyvinylidene difluoride, or a mixture thereof.

14. The process of claim 11, wherein said membrane comprises polypropylene.

15. The process of any one of claims 12 to 14, wherein after passing said composition through said membrane, said aqueous phase is separated from said organic phase, said aluminum ions are recovered in said aqueous phase and said aqueous phase is treated with a base.

16. The process of claim 15, wherein said base comprises NaOH, KOH, or a mixture thereof.

17. The process of claim 15, wherein said base comprises NaOH.
18. The process of any one of claims 15 to 17, wherein said aqueous phase is treated with said base so as to obtain a pH of at least about 4.

19. The process of any one of claims 15 to 18, further comprising a separation by filtration to obtain Al(OH)_3.

20. The process of claim 19, further comprising washing said Al(OH)_3.

21. The process of any one of claims 15 to 20, further comprising converting Al(OH)_3 into Al_2O_3.

22. The process of claim 21, wherein conversion of Al(OH)_3 into Al_2O_3 is carried out at a temperature of about 800 °C to about 1200 °C.

23. The process of any one of claims 15 to 23, further comprising treating said organic phase with HCl and isolating said iron ions in the form of Fe^{3+}.

24. The process of claim 1, wherein said composition comprises an acidic aqueous phase comprising iron ions and an organic phase comprising aluminum ions complexed with said extracting agent, and wherein said aluminum ions are recovered by separating said aqueous phase from said organic phase.

25. The process of claim 24, wherein said aqueous phase has a pH of about 2.5 to about 3.5.

26. The process of claim 24 or 25, wherein said extracting agent is a phosphinic acid or a derivative thereof.

27. The process of claim 24 or 25, wherein said extracting agent is bis(2,4,4-trimethylpentyl) phosphinic acid.
28. The process of any one of claims 24 to 27, wherein said extracting agent has a concentration of about 10 % to about 25 % v/v with respect to said organic solvent.

29. The process of any one of claims 24 to 27, wherein said extracting agent has a concentration of about 20 % v/v with respect to said organic solvent.

30. The process of any one of claims 24 to 29, wherein said organic solvent is chosen from C₅-C₁₂ alkanes and mixtures thereof.

31. The process of any one of claims 24 to 29, wherein said organic solvent is heptane.

32. The process of any one of claims 24 to 31, wherein said composition has a volumic ratio aqueous phase : organic phase of about 1:1 to about 1:3.

33. The process of any one of claims 24 to 31, wherein said organic phase and said aqueous phase are separated by means of a membrane.

34. The process of claim 33, wherein said membrane is a hollow fiber membrane.

35. The process of claim 34, wherein said membrane comprises polypropylene, polyvinylidene difluoride, or a mixture thereof.

36. The process of claim 34, wherein said membrane comprises polypropylene.

37. The process of any one of claims 24 to 36, wherein said composition is at a temperature of about 30 °C to about 50 °C.
38. The process of any one of claims 24 to 37, wherein said composition is at a temperature of about 35 °C to about 45 °C.

39. The process of any one of claims 24 to 37, wherein after passing said composition through said membrane, said aqueous phase is separated from said organic phase, said complexed aluminum ions are recovered in said organic phase, said organic phase being then treated with HCl so as to obtain an aqueous composition comprising said aluminum ions.

40. The process of claim 39, wherein aluminum ions are converted into Al(OH)$_3$ by adding contacting it with a base.

41. The process of claim 40, wherein said base comprises NaOH, KOH, or a mixture thereof.

42. The process of claim 40, wherein said base comprises NaOH.

43. The process of any one of claims 40 to 42, wherein said aqueous composition is treated with said base so as to obtain a pH of at least about 4.

44. The process of claim 43, further comprising a separation by filtration at to obtain Al(OH)$_3$.

45. The process of claim 44, further comprising washing said Al(OH)$_3$.

46. The process of any one of claims 43 to 45, further comprising converting Al(OH)$_3$ into Al$_2$O$_3$.

47. The process of claim 46, wherein conversion of Al(OH)$_3$ into Al$_2$O$_3$ is carried out at a temperature of about 800 °C to about 1200 °C.
48. A composition comprising aluminum ions, iron ions, an organic solvent and an extracting agent adapted to form an organometallic complex substantially selectively with said iron ions or with said aluminum ions which is soluble in said organic solvent.

49. A composition comprising an acidic aqueous phase comprising aluminum ions and an organic phase comprising iron ions complexed with an extracting agent.

50. A composition comprising an acidic aqueous phase comprising iron ions and an organic phase comprising aluminum ions complexed with an extracting agent.

51. A process for at least partially separating aluminum ions from iron ions comprised in a composition, said process comprising substantially selectively precipitating at least a portion of said iron ions in basic conditions in which the pH is of at least 10.

52. The process of claim 51, wherein said iron ions are precipitated from a basic aqueous composition comprising NaOH.

53. The process of claim 51, wherein said iron ions are precipitated from a basic aqueous composition comprising KOH.

54. The process of claim 51, wherein a base is reacted with said composition so as to obtain a mixture in which the pH is of at least 10, and then, said at least portion of precipitated iron ions are separated from the rest of said mixture.
55. The process of claim 54, wherein said precipitated iron ions are separated from the rest of said mixture by carrying out a filtration, a decantation, a centrifugation, or combinations thereof.

56. The process of claim 54 or 55, wherein said base is chosen from KOH, NaOH, and mixtures thereof.

57. The process of claim 54 or 55, wherein said base is NaOH.

58. The process of claim 54 or 55, wherein said base is KOH.

59. The process of any one of claims 54 to 58, further comprising rinsing the obtained precipitated iron ions with a basic solution.

60. The process of claim 59, wherein the basic solution is NaOH or KOH having a concentration of about 0.01 M to about 0.02 M.

61. The process of any one of claims 51 to 60, wherein said pH is at least 11.

62. The process of any one of claims 51 to 60, wherein said pH is at least 12.

63. The process of any one of claims 51 to 60, wherein said pH is about 10.8 to about 11.2.

64. The process of any one of claims 51 to 60, wherein said pH is about 11.5 to about 12.5.

65. The process of any one of claims 51 to 64, further comprising purifying the precipitated iron ions by means of a hollow fiber membrane.
66. A process for extracting aluminum from an aluminum ore, said process comprising:

  - leaching said aluminum ore with an acid so as to obtain a leachate and a solid residue;

  - removing at least a portion of iron ions contained in said leachate by:

    (i) substantially selectively precipitating said at least portion of said iron ions in basic conditions in which the pH is of at least 10, so as to obtain an aluminum enriched composition; or

    (ii) substantially selectively complexing said at least portion of said iron ions with an extracting agent adapted to form an organometallic complex substantially selectively with said iron ions so as to obtain an aluminum enriched composition.

67. The process of claim 66, wherein said acid is HCl.

68. The process of claim 66, wherein said aluminum ore is leached with HCl at a temperature of at least 80 °C.

69. The process of claim 66, wherein said aluminum ore is leached with HCl at a temperature of at least 90 °C.

70. The process of claim 66, wherein said aluminum ore is leached with HCl at a temperature of about 100 °C to about 110 °C.

71. The process of any one of claims 67 to 70, wherein said acid is HCl having a concentration of about 6 M.

72. The process of any one of claims 66 to 71, wherein the aluminum ore / acid ratio is about 1 / 10 in weight by volume.
73. The process of any one of claims 66 to 72, wherein removal of said at least portion of iron ions is carried out by precipitating said iron ions from a basic aqueous composition comprising NaOH.

74. The process of any one of claims 66 to 72, wherein removal of said at least portion of iron ions is carried out by precipitating said iron ions from a basic aqueous composition comprising KOH.

75. The process of any one of claims 66 to 72, wherein removal of said at least portion of iron ions is carried out by reacting said leachate with a base in order to obtain a pH of at least 10 and precipitating said iron ions.

76. The process of claim 75, wherein said precipitated iron ions are separated from the rest of said leachate by carrying out a filtration, a decantation, a centrifugation, or mixtures thereof.

77. The process of claim 75 or 76, wherein said base is chosen from KOH, NaOH, and mixtures thereof.

78. The process of claim 75 or 76, wherein said base is NaOH.

79. The process of claim 75 or 76, wherein said base is KOH.

80. The process of any one of claims 75 to 79, further comprising rinsing the obtained precipitated iron ions with a basic solution.

81. The process of claim 80, wherein the basic solution is NaOH or KOH having a concentration of about 0.01 M to about 0.02 M.

82. The process of any one of claims 75 to 81 wherein said pH is at least 11.
83. The process of any one of claims 75 to 81 wherein said pH is at least 12.

84. The process of any one of claims 75 to 81 wherein said pH is about 10.8 to about 11.2.

85. The process of any one of claims 75 to 81 wherein said pH is about 11.5 to about 12.5.

86. The process of any one of claims 66 to 85, further comprising purifying the precipitated iron ions by means of a hollow fiber membrane.

87. The process of any one of claims 66 to 86, wherein removal of said at least portion of iron ions is carried out by reacting said leachate, under acidic conditions, with said extracting agent and an organic solvent in order to obtain a composition comprising an acidic aqueous phase comprising aluminum ions and an organic phase comprising iron ions complexed with said extracting agent, said aluminum enriched composition being obtained by separating said aqueous phase from said organic phase.

88. The process of claim 87, wherein said aqueous phase has a pH of about 1 to about 2.5.

89. The process of claim 87, wherein said aqueous phase has a pH of about 2.

90. The process of any one of claims 87 to 89, wherein said extracting agent is chosen from di-2-ethylhexyl phosphoric acid (HDEHP), bis(2,4,4-trimethylpentyl) phosphinic acid and 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester).
91. The process of any one of claims 87 to 90, wherein said extracting agent has a concentration of about 0.5 M to about 1.5 M in said organic phase.

92. The process of any one of claims 87 to 90, wherein said extracting agent has a concentration of about 1 M in said organic phase.

93. The process of any one of claims 87 to 90, wherein said organic solvent is chosen from C\textsubscript{5}-C\textsubscript{12} alkanes and mixtures thereof.

94. The process of any one of claims 87 to 90, wherein said organic solvent is heptane.

95. The process of any one of claims 87 to 94, wherein said composition has a volumic ratio organic phase : aqueous phase of about 1:1.

96. The process of any one of claims 87 to 95, wherein said organic phase and said aqueous phase are separated by means of a filtration membrane.

97. The process of claim 96, wherein said membrane is a hollow fiber membrane.

98. The process of claim 97, wherein said membrane comprises polypropylene, polyvinylidene difluoride, or a mixture thereof.

99. The process of claim 97, wherein said membrane comprises polypropylene.

100. The process of any one of claims 96 to 99, wherein after passing said composition through said membrane, said aqueous phase is separated from said organic phase, said aluminum ions are recovered in said aqueous phase and said aqueous phase is treated with a base.
101. The process of claim 100, wherein said base comprises NaOH, KOH, or a mixture thereof.

102. The process of claim 100, wherein said base comprises NaOH.

103. The process of any one of claims 100 to 102, wherein said aqueous phase is treated with said base so as to obtain a pH of at least about 4.

104. The process of any one of claims 100 to 103, further comprising a separation by filtration to obtain Al(OH)₃.

105. The process of claim 104, further comprising washing said Al(OH)₃.

106. The process of any one of claims 66 to 105, wherein said aluminum ore is crushed and roasted before being leached.

107. The process of any one of claims 66 to 106, wherein before removal of said iron ions, said leachate is treated with a base.

108. The process of any one of claims 66 to 107, wherein before removal of said iron ions, said leachate is distilled so as to reduce its volume.

109. The process of any one of claims 66 to 108, further comprising at least partially recovering said aluminum ions present in said aluminum enriched composition.

110. The process of claim 109, wherein said aluminum enriched composition is treated with an extracting agent adapted to form an organometallic complex substantially selectively with said aluminum ions in the presence of an organic solvent and an acid solution in order to form a composition comprising an acidic aqueous phase comprising impurities and an organic phase comprising aluminum
ions complexed with said extracting agent, and wherein said aluminum ions are recovered by separating said aqueous phase from said organic phase.

111. The process of claim 110, wherein said aqueous phase has a pH of about 2.5 to about 3.5.

112. The process of claim 110 or 111, wherein said extracting agent is a phosphinic acid or a derivative thereof.

113. The process of claim 110 or 111, wherein said extracting agent is bis(2,4,4-trimethylpentyl) phosphinic acid.

114. The process of any one of claims 110 to 113, wherein said extracting agent has a concentration of about 10 % to about 25 % v/v with respect to said organic solvent.

115. The process of any one of claims 110 to 113, wherein said extracting agent has a concentration of about 20 % v/v with respect to said organic solvent.

116. The process of any one of claims 110 to 115, wherein said organic solvent is chosen from C_5- C_{12} alkanes and mixtures thereof.

117. The process of any one of claims 110 to 115, wherein said organic solvent is heptane.

118. The process of any one of claims 110 to 117, wherein said composition has a volumic ratio aqueous phase : organic phase of about 1:1 to about 1:3.
119. The process of any one of claims 110 to 118, wherein said organic phase and said aqueous phase are separated by means of a membrane.

120. The process of claim 119, wherein said membrane is a hollow fiber membrane.

121. The process of claim 120, wherein said membrane comprises polypropylene, polyvinylidene difluoride, or a mixture thereof.

122. The process of claim 120, wherein said membrane comprises polypropylene.

123. The process of any one of claims 110 to 122, wherein said composition is at a temperature of about 30 °C to about 50 °C.

124. The process of any one of claims 110 to 122, wherein said composition is at a temperature of about 35 °C to about 45 °C.

125. The process of any one of claims 119 to 124, wherein after passing said composition through said membrane, said aqueous phase is separated from said organic phase, said complexed aluminum ions are recovered in said organic phase, said organic phase being then treated with HCl so as to obtain an aqueous composition comprising said aluminum ions.

126. The process of claim 125, wherein aluminum ions are converted into Al(OH)₃ by contacting it with a base.

127. The process of claim 104, 105, or 126, further comprising converting Al(OH)₃ into Al₂O₃.
128. The process of claim 127, wherein conversion of $\text{Al(OH)}_3$ into $\text{Al}_2\text{O}_3$ is carried out at a temperature of about 800 °C to about 1200 °C.
**RAW ARGILITE**

Option 1: Leaching at room temperature HCl (12 M)

**Preparation of argilite**

Roasting

**Acid leaching**

Hot leaching HCl (6 M)

Partial distillation

Enrichment of HCl recovered with gaseous HCl gazex or HCl (12 M)

HCl recovered

Separation

Concentrated leachate + washing water

Argilite impoverished in metals (resin)

Volume reduction with more than 90% by distillation

**Option 3**

Precipitation of Fe at pH > 10

Refining by liquid-liquid extraction

Option 2

Fe\textsuperscript{3+} ion rich concentrate

Al rich liquid

pH adjustment at 3-4

Refining by liquid-liquid extraction

Al\textsuperscript{3+} ions rich pure concentrate

Formation of Al(OH)\textsubscript{3}

**Formation of Al\textsubscript{2}O\textsubscript{3} by roasting**

**Iron removal**

**Aluminum recovery**

Fig. 1
**INTERNATIONAL SEARCH REPORT**

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC: C22B 21/00 (2006.01), C22B 3/10 (2006.01), C22B 3/22 (2006.01), C22B 3/38 (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: C22B 21/00, C22B 3/26, C22B 3/38, C22B 3/44

USPC: 423/112, 423/139, 423/132, 423/122, 423/140, 75

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)

CPD, WEST, Espacenet, CAPlus, Google Scholar

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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<td>US 3473919 (METCALFE et al.) 21 October 1969 (21-10-1969)</td>
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[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  
'E' earlier application or patent but published on or after the international filing date  
'L' document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)  
'O' document referring to an oral disclosure, use, exhibition or other means  
'P' document published prior to the international filing date but later than the priority date claimed

Date of the actual completion of the international search  
30 July 2008 (30-07-2008)

Date of mailing of the international search report  
11 August 2008 (11-08-2008)

Name and mailing address of the ISA/CA  
Canadian Intellectual Property Office  
Place du Portage I, C1 14 - 1st Floor, Box PCT  
50 Victoria Street  
Gatineau, Quebec K1A 0C9  
Facsimile No.: 001-819-953-2476

Authorized officer  
Jay Fothergill  
819-997-4842
### INTERNATIONAL SEARCH REPORT

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

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

1. [ ] Claim Nos  
   because they relate to subject matter not required to be searched by this Authority, namely

2. [ ] Claim Nos  
   because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically

3. [ ] Claim Nos  
   because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6 4(a)

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

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

Invention 1 claims 1-50, 66 (option ii) and 87-105 define processes and compositions featuring an extracting agent that complexes with one of aluminum and iron in a mixture thereof.

Invention 2 claims 51-65, 66 (option i) and 73-86 define processes for precipitating iron in basic conditions at a pH of at least 10 from a composition containing both

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

2. [X] As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

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

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

**Remark on Protest**  
[ ] The additional search fees were accompanied by the applicant’s protest and, where applicable, the payment of a protest fee.

[ ] The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

[ ] No protest accompanied the payment of additional search fees.
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