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(54) **Titre : PROCÉDES D'OBTENTION D'HEMATITE**  
(54) **Title: METHODS FOR PREPARING HEMATITE**

(57) **Abrégé/Abstract:**

There is provided a method for preparing hematite. The method comprises obtaining hematite from a basic aqueous composition comprising at least one precipitated iron ion, having a pH of about 10.5 to about 13 and being at temperature of about 50 °C to about 150 °C, by reacting the composition with hematite, thereby promoting, catalyzing and/or enhancing formation of the hematite. For example, the basic aqueous composition is obtained by leaching an iron-containing material so as to obtain a leachate and a solid residue; separating the leachate from the solid residue; and reacting the leachate with a base. It can alternatively be obtained by leaching the iron-containing material so as to obtain a leachate and a solid residue; optionally removing the at least a portion of the at least one iron ion from the leachate; separating the leachate from the solid residue; and reacting the leachate with a base.



## ABSTRACT

There is provided a method for preparing hematite. The method comprises obtaining hematite from a basic aqueous composition comprising at least one precipitated iron ion, having a pH of about 10.5 to about 13 and being at temperature of about 50 °C to about 150 °C, by reacting the composition with hematite, thereby promoting, catalyzing and/or enhancing formation of the hematite. For example, the basic aqueous composition is obtained by leaching an iron-containing material so as to obtain a leachate and a solid residue; separating the leachate from the solid residue; and reacting the leachate with a base. It can alternatively be obtained by leaching the iron-containing material so as to obtain a leachate and a solid residue; optionally removing the at least a portion of the at least one iron ion from the leachate; separating the leachate from the solid residue; and reacting the leachate with a base.

## METHODS FOR PREPARING HEMATITE

### TECHNICAL FIELD

[0001] The present disclosure relates to improvements in the field of chemistry applied to the synthesis of iron-based products. For example, such methods are useful for the preparation of hematite.

### BACKGROUND OF THE DISCLOSURE

[0002] Hematite has been used as a colorant for centuries. It is the most common type of naturally occurring iron oxide mineral. Examples of hematites include hematites, pyrites, and magnetites, which are respectively red-colored, yellow-colored, and black-colored. Hematites are mostly prepared as synthetic products, and thus are used in various fields as pigments having clear color tones and excellent durability, being inexpensive and having low toxicity and high stability. In particular, well-known synthetic hematite pigments include red or red brown-colored hematite particle powder ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> or micaceous iron oxide (MIO)), yellow or deep brown-colored maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>) particle powder, and black-colored magnetite (FeO<sub>x</sub>-Fe<sub>2</sub>O<sub>3</sub> where  $0 < x \leq 1$ ). Many of the processes proposed so far for preparing such products comprise at least one drawbacks such as being not cost effective, not being environmental friendly or being complicated.

[0003] There is thus a need for at least providing an alternative to the existing solutions for preparing hematites. Moreover, there would be a need for valorizing certain waste materials and at least partially convert them into hematite.

### SUMMARY OF THE DISCLOSURE

[0004] According to one aspect, there is provided a method for preparing hematite. The method comprises obtaining the hematite from a basic aqueous composition comprising at least one precipitated iron ion, having a pH of about 10.5 to about 12 and being at a temperature of about 70 °C to about

120 °C, by reacting the composition with a predetermined quantity of hematite, thereby promoting, catalyzing and/or enhancing formation of the hematite.

**[0005]** According to another aspect, there is provided a method for preparing hematite. The method comprises obtaining the hematite from a basic aqueous composition comprising at least one precipitated iron ion, having a pH of about 10.5 to about 13 and being at a temperature of about 50 °C to about 150 °C, by reacting the composition with hematite, thereby promoting, catalyzing and/or enhancing formation of the hematite.

**[0006]** According to one aspect, there is provided a method for preparing hematite. The method comprises obtaining the hematite from a basic aqueous composition comprising at least one precipitated iron ion, having a pH of about 10.5 to about 12 and being at a temperature of about 70 °C to about 120 °C, by reacting the composition with a predetermined quantity of hematite, thereby promoting, catalyzing and/or enhancing formation of the hematite.

**[0007]** According to another aspect, there is provided a method for separating iron ions from aluminum ions contained in a basic aqueous composition, the method comprising :

obtaining a basic aqueous composition comprising iron ions and aluminum ions and having a pH of about 10.5 to about 12 and a temperature of about 70 °C to about 120 °C;

reacting the composition with a predetermined quantity of hematite so as to promote, catalyze and/or enhance formation of hematite and to obtain a liquid phase comprising the aluminum ions and a solid phase comprising the so-formed hematite; and

separating the liquid phase from the solid phase.



**[0008]** According to another aspect, there is provided a method for separating iron ions from aluminum ions contained in a basic aqueous composition, the method comprising :

obtaining a basic aqueous composition comprising the iron ions and the aluminum ions and having a pH of about 10.5 to about 13 and a temperature of about 50 °C to about 150 °C;

reacting the composition with hematite so as to promote, catalyze and/or enhance formation of hematite and to obtain a liquid phase comprising the aluminum ions and a solid phase comprising the so-formed hematite; and

separating the liquid phase from the solid phase.

**[0009]** According to another aspect, there is provided a method for separating iron ions from aluminum ions contained in a basic aqueous composition, the method comprising :

obtaining the basic aqueous composition comprising the iron ions and the aluminum ions and having a pH of about 10.5 to about 13 and a temperature of about 50 °C to about 150 °C;

reacting the basic aqueous composition with hematite so as to promote, catalyze and/or enhance formation of hematite and to obtain a liquid phase comprising the aluminum ions and a solid phase comprising the so-formed hematite generated with at least a portion of the iron ions; and

separating the liquid phase from the solid phase.

**[0010]** According to another aspect, there is provided a method for separating iron ions from aluminum ions contained in a basic aqueous composition, the method comprising :

reacting the basic aqueous composition comprising the iron ions and the aluminum ions with a seeding agent under conditions suitable for

promoting, catalyzing and/or enhancing formation of hematite under the form of a precipitate, thereby obtaining a liquid phase and a solid phase; and

separating the liquid phase from the solid phase.

[0011] According to another aspect, there is provided a method for separating iron ions from aluminum ions contained in a basic aqueous composition, the method comprising :

reacting the basic aqueous composition comprising the iron ions and the aluminum ions with a seeding agent under conditions suitable for at least partially converting the iron ions into hematite under the form of a precipitate, thereby obtaining a liquid phase and a solid phase; and

separating the liquid phase from the solid phase.

[0012] According to another aspect, there is provided a method for separating iron from aluminum contained in a basic aqueous composition, the method comprising :

reacting the basic aqueous composition comprising the iron and the aluminum with hematite under conditions suitable for at least partially converting the iron into hematite under the form of a precipitate, thereby obtaining a liquid phase and a solid phase; and separating the liquid phase from the solid phase.

#### **DETAILED DESCRIPTION OF VARIOUS EMBODIMENTS**

[0013] Further features and advantages will become more readily apparent from the following description of various embodiments as illustrated by way of examples only and in a non-limitative manner.

[0014] The term "hematite" as used herein refers, for example, to a compound comprising  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. The compound can also comprises  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>,  $\beta$ -FeO.OH or mixtures thereof.

[0015] 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  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ , or a mixture thereof.

**[0016]** 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  $\text{Al}^{3+}$ .

**[0017]** 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  $\text{Al}^{3+}$ .

**[0018]** 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  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ , or a mixture thereof.

**[0019]** 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  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ , or a mixture thereof.

**[0020]** The term “suitable” as used herein means that the selection of the particular conditions would depend on the specific manipulation to be performed, but the selection would be well within the skill of a person trained in the art. All process/method elements described herein are to be conducted under conditions sufficient to provide the desired product. A person skilled in the art would understand that all reaction conditions, including, for example, reaction solvent, reaction time, reaction temperature, reaction pressure, reactant ratio, etc, can be varied to optimize the yield of the desired product and it is within their skill to do so.

**[0021]** 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  $\pm 5\%$  or at least  $\pm 10\%$  of the



modified term if this deviation would not negate the meaning of the word it modifies.

**[0022]** The expression “at least substantially maintained” as used herein when referring to a value of a pH or a pH range that is maintained when reacting the basic aqueous composition with hematite refers to maintaining the value of the pH or the pH range at least 75, 80, 85, 90, 95, 96, 97, 98 or 99 % of the time during such a reaction.

**[0023]** The expression “at least substantially maintaining” as used herein when referring to a value of a pH or a pH range that is maintained when reacting the basic aqueous composition with hematite refers to maintaining the value of the pH or the pH range at least 75, 80, 85, 90, 95, 96, 97, 98 or 99 % of the time during such a reaction.

**[0024]** The expression “at least substantially maintaining” as used herein when referring to a value of a temperature or a temperature range that is maintained when reacting the basic aqueous composition with hematite refers to maintaining the value of the temperature or the temperature range at least 75, 80, 85, 90, 95, 96, 97, 98 or 99 % of the time during the process or the portion thereof.

**[0025]** The expression “at least substantially maintained” as used herein when referring to a value of a temperature or a temperature range that is maintained when reacting the basic aqueous composition with hematite refers to maintaining the value of the temperature or the temperature range at least 75, 80, 85, 90, 95, 96, 97, 98 or 99 % of the time during the process or the portion thereof.

**[0026]** For example, the methods can further comprise precipitating the aluminum ions from the liquid phase by adjusting pH of the liquid phase at a value of about 7 to about 11, about 8 to about 10.5, about 9 to about 10, about 9.2 to about 9.8, or about 9.5.

**[0027]** For example, aluminum ions can be precipitated from the liquid phase by reacting it with an acid. The acid used can be HCl, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub> or mixtures thereof.



**[0028]** For example, precipitating the aluminum ions can be carried out at a temperature of about 40 °C to about 80 °C, about 50 °C to about 70 °C or about 60 °C to about 70 °C. For example, precipitating the aluminum ions can be carried out at by at least substantially maintaining the temperature.

**[0029]** For example, the methods can further comprise adding a precipitating agent effective for facilitating precipitation of the aluminum ions. For example, the precipitating agent is a polymer such as an acrylamide polymer.

**[0030]** For example, the basic aqueous composition, before being reacted with the hematite, can comprises at least one precipitate that comprises iron under the form of  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$ , or a mixture thereof.

**[0031]** For example, the basic aqueous composition, before being reacted with the hematite, can comprise at least one precipitate that comprises  $\text{Fe}(\text{OH})_3$ ,  $\text{Fe}(\text{OH})_2$ , or a mixture thereof.

**[0032]** For example, the basic aqueous composition, before being reacted with the hematite, comprises iron ions under the form of  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$ , or a mixture thereof.

**[0033]** For example, the hematite can be reacted with the basic aqueous composition under agitation.

**[0034]** For example, the basic aqueous composition can have a temperature of about 50 °C to about 70 °C, about 65 °C to about 75 °C, about 70 °C to about 80 °C, about 70 °C to about 100 °C, about 75 °C to about 110 °C, about 80 °C to about 100 °C, about 85 °C to about 95 °C, about 87 °C to about 93 °C, about 70 °C to about 120 °C, about 90 °C to about 100 °C, about 70 °C, about 75 °C, about 80 °C, about 85 °C, about 90 °C, or about 95 °C.

**[0035]** For example, the basic aqueous composition can be reacted with the hematite by at least substantially maintaining the basic aqueous composition at the temperature.

**[0036]** For example, the reaction between the basic aqueous composition and hematite can be carried out by at least substantially maintaining a temperature of about 50 °C to about 150 °C, about 50 °C to about 70 °C, about 65 °C to about 75 °C, about 70 °C to about 80 °C, about 70 °C to about 100 °C, about 75 °C to about 110 °C, about 80 °C to about 100 °C, about 85 °C to about 95 °C, about 87 °C to about 93 °C, about 70 °C to about 120 °C, about 90 °C to about 100 °C, about 70 °C, about 75 °C, about 80 °C, about 85 °C, about 90 °C, or about 95 °C.

**[0037]** For example, the basic aqueous composition can have a pH of about 10.8 to about 11.8, about 11 to about 12, about 11.5 to about 12.5, about 11.0 to about 11.6, about 11.2 to about 11.5, about 10.5 to about 12, about 11.5 to about 12.5, or about 11.8 to about 12.2, about 11.0, about 11.1, about 11.2, about 11.3, about 11.4, about 11.5, about 11.6, about 11.7, about 11.8, about 11.9, or about 12.0.

**[0038]** For example, the reaction between the basic aqueous composition and hematite can be carried out by at least substantially maintaining the pH.

**[0039]** For example, the reaction between the basic aqueous composition and hematite can be carried out by at least substantially maintaining a pH of about 10.5 to about 13, about 10.8 to about 11.8, about 11 to about 12, about 11.5 to about 12.5, about 11.0 to about 11.6, about 11.2 to about 11.5, about 10.5 to about 12, about 11.5 to about 12.5, about 11.8 to about 12.2, about 11.0, about 11.1, about 11.2, about 11.3, about 11.4, about 11.5, about 11.6, about 11.7, about 11.8, about 11.9, or about 12.0.

**[0040]** For example, about 0.25 to about 25 g, about 1 to about 20 g, about 1 to about 10 g, about 1.5 to about 5.5 g, or about 2 to about 15 g of hematite can be used per liter of the basic aqueous composition.

**[0041]** For example, the basic aqueous composition can have a concentration of Fe of about 0.5 to about 10 g/L, about 1 to about 7 g/L, or about 1.5 to about 5.5 g/L.

**[0042]** For example, hematite can be into the basic aqueous composition. For example, hematite can be added at a molar ratio hematite / total amount of iron contained in the basic aqueous composition of about 0.005 to about 0.5 or about 0.01 to about 0.1.

**[0043]** For example, the basic aqueous composition can be obtained by :

leaching an iron-containing material comprising iron and aluminum with an acid so as to obtain a leachate comprising the iron ions and the aluminum ions and a solid residue;

separating the leachate from the solid residue; and

reacting the leachate with a base.

**[0044]** For example, the basic aqueous composition can be obtained by :

leaching an iron-containing material comprising iron and aluminum with an acid so as to obtain a leachate comprising the iron ions and the aluminum ions and a solid residue;

optionally removing at least a portion of the iron ions from the leachate;

separating the leachate from the solid residue; and

reacting the leachate with a base.

**[0045]** For example, the base can be KOH, NaOH,  $\text{Ca(OH)}_2$ , CaO, MgO,  $\text{Mg(OH)}_2$ ,  $\text{CaCO}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{NaHCO}_3$ , or mixtures thereof.

**[0046]** For example, the base can have a concentration of about 2 to about 20 M, about 2.5 M to about 10 M or about 3 to about 4 M.

**[0047]** For example, the base can have a concentration of about 30 to about 60 weight %, about 35 to about 55 weight %.



**[0048]** For example, the leachate and a first portion of the base can be added simultaneously into a reactor comprising a second portion of the base. For example, the basic aqueous composition can be reacted with the hematite by at least substantially maintaining the basic aqueous composition at the pH. For example, the basic aqueous composition can be at least substantially maintained at the pH by reacting it with a further amount of the base.

**[0049]** For example, reacting the leachate with the base can generate precipitation of at least a portion of the iron ions into  $\text{Fe}(\text{OH})_3$ ,  $\text{Fe}(\text{OH})_2$ , or a mixture thereof.

**[0050]** For example, upon reacting hematite with the basic aqueous composition, at least a portion of the  $\text{Fe}(\text{OH})_3$ ,  $\text{Fe}(\text{OH})_2$ , or the mixture thereof can be converted into hematite.

**[0051]** For example, iron can be present in the basic aqueous composition, before reacting it with the hematite, under the form of solubilized ions, a precipitate or a mixture thereof.

**[0052]** For example, the basic aqueous composition can comprise, before reacting it with the hematite, solubilized  $\text{Fe}^{3+}$  ions, solubilized  $\text{Fe}^{2+}$  ions or a mixture thereof.

**[0053]** For example, the basic aqueous composition can comprise, before reacting it with the hematite, precipitated iron under the form of  $\text{Fe}(\text{OH})_3$ ,  $\text{Fe}(\text{OH})_2$  or a mixture thereof.

**[0054]** For example, the conditions suitable for at least partially converting the iron into hematite under the form of a precipitate can comprise reacting the basic aqueous composition with hematite at a temperature of about 50 °C to about 150 °C, about 50 °C to about 70 °C, about 65 °C to about 75 °C, about 70 °C to about 80 °C, about 70 °C to about 100 °C, about 75 °C to about 110 °C, about 80 °C to about 100 °C, about 85 °C to about 95 °C, about 87 °C to about 93 °C, about 70 °C to about 120 °C, about 90 °C to

about 100 °C, about 70 °C, about 75 °C, about 80 °C, about 85 °C, about 90 °C, or about 95 °C.

**[0055]** For example, the conditions suitable for at least partially converting the iron into hematite under the form of a precipitate can comprise at least substantially maintaining the temperature while reacting the basic aqueous composition with hematite.

**[0056]** For example, the conditions suitable for at least partially converting the iron into hematite under the form of a precipitate can comprise reacting the basic aqueous composition with hematite at a pH of about 10.5 to about 13, about 10.8 to about 11.8, about 11 to about 12, about 11.5 to about 12.5, about 11.0 to about 11.6, about 11.2 to about 11.5, about 10.5 to about 12, about 11.5 to about 12.5, about 11.8 to about 12.2, about 11.0, about 11.1, about 11.2, about 11.3, about 11.4, about 11.5, about 11.6, about 11.7, about 11.8, about 11.9, or about 12.0.

**[0057]** For example, the conditions suitable for at least partially converting the iron into hematite under the form of a precipitate can comprise at least substantially maintaining the pH while reacting the basic aqueous composition with hematite.

**[0058]** For example, the conditions suitable for at least partially converting the iron into hematite under the form of a precipitate can comprise reacting about 0.25 to about 25 g of, about 0.5 to about 25 g, about 1 to about 20 g, about 1 to about 10 g, about 1.5 to about 5.5 g, or about 2 to about 15 g of hematite per liter of the basic aqueous composition.

**[0059]** For example, the precipitated aluminum ions can be under the form of  $\text{Al}(\text{OH})_3$ .

**[0060]** For example, the methods can further comprise converting  $\text{Al}(\text{OH})_3$  into  $\text{Al}_2\text{O}_3$ . Such a conversion can be done, for example, in various manner including by those as described in WO 2008/141423.

**[0061]** For example, the methods can further comprise converting  $\text{Al}(\text{OH})_3$  into  $\text{AlCl}_3$ . Such a conversion can be done, for example, by reacting  $\text{Al}(\text{OH})_3$  with  $\text{HCl}$ .

**[0062]** For example, the methods can further comprise converting  $\text{AlCl}_3$  into  $\text{Al}_2\text{O}_3$ . Such a conversion can be done, for example, in various manner including by thermal decomposition and calcination. For example, the decomposition/calcination can be done in a rotary furnace. For example, it can be done at variable speed where the temperature gradually rises from  $300^\circ\text{C}$  at the entry to reach around  $1250^\circ\text{C}$  at its maximum.

**[0063]** For example, the at least one precipitated iron ion can be chosen from  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$ , and a mixture thereof.

**[0064]** For example, the at least one precipitated iron ion can be under the form of  $\text{Fe}(\text{OH})_2$ ,  $\text{Fe}(\text{OH})_3$ , or a mixture thereof.

**[0065]** For example, the predetermined quantity of hematite can be added to the basic aqueous composition, over a predetermined period of time, optionally under agitation.

**[0066]** For example, the predetermined quantity of hematite can be added at a molar ratio hematite / the at least one iron ion of about 0.005 to about 0.5 or about 0.01 to about 0.1.

**[0067]** For example, the basic aqueous composition can be obtained by :

leaching an aluminum-containing ore comprising the at least one iron ion (or comprising iron) with an acid so as to obtain a leachate and a solid residue;

separating the leachate from the solid residue;

and

reacting the leachate with a base.

**[0068]** For example, the basic aqueous composition can be obtained by :



leaching an aluminum-containing ore comprising the at least one iron ion (or comprising iron) with an acid so as to obtain a leachate and a solid residue;

optionally removing at least a portion of the iron ions from the leachate;

separating the leachate from the solid residue;  
and

reacting the leachate with a base.

**[0069]** For example, the acid used for leaching can be HCl, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub> or mixtures thereof.

**[0070]** The iron-containing material can be an aluminum-containing material. The aluminum-containing material can be an aluminum-containing ore. For example, clays, argillite, mudstone, beryl, cryolite, garnet, spinel, bauxite, or mixtures thereof can be used as starting material. The aluminum-containing material can also be a recycled industrial aluminum-containing material such as slag. The aluminum-containing material can also be red mud or fly ashes.

**[0071]** The acid used for leaching aluminum-containing ore can be HCl, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub> or mixtures thereof. More than one acid can be used as a mixture or separately. Solutions made with these acids can be used at various concentration. For example, concentrated solutions can be used. For example, 6 M or 12 M HCl can be used. For example, up to 100 % wt H<sub>2</sub>SO<sub>4</sub> can be used.

**[0072]** The leaching can be carried out under pressure. For example, the pressure can be about 10 to about 300 psig, about 25 to about 250 psig, about 50 to about 200 psig or about 50 to about 150 psig. The leaching can be carried out for about 30 minutes to about 5 hours. It can be carried out at a

temperature of about 60 to about 300 °C, about 75 to about 275 °C or about 100 to about 250 °C.

**[0073]** After the leaching, various bases can be used for raising up the pH such as KOH, NaOH,  $\text{Ca(OH)}_2$ , CaO, MgO,  $\text{Mg(OH)}_2$ ,  $\text{CaCO}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{NaHCO}_3$ , or mixtures thereof.

**[0074]** For example, iron ions can be precipitated. When precipitating iron ions, the iron ions can be precipitated by means of an ionic precipitation and they can precipitate in the form of various salts, hydroxides or hydrates thereof. For example, the iron ions can be precipitated as  $\text{Fe(OH)}_3$ ,  $\text{Fe(OH)}_2$ , hematite, goetite, jarosite or hydrates thereof.

**[0075]** For example, aluminum ions can be precipitated. When precipitating aluminum ions, the aluminum ions can be precipitated by means of an ionic precipitation and they can precipitate in the form of various salts, (such as chlorides, sulfates) or hydroxides or hydrates thereof. For example, the aluminum ions can be precipitated as  $\text{Al(OH)}_3$ ,  $\text{AlCl}_3$ ,  $\text{Al}_2(\text{SO}_4)_3$ , or hydrates thereof.

**[0076]** The methods of the present disclosure can be effective for treating various aluminum-containing ores. For example, clays, argillite, mudstone, beryl, cryolite, garnet, spinel, bauxite, or mixtures thereof can be used as starting material.

**[0077]** The leaching can be carried out at a pH of about 0.5 to about 2.5, about 0.5 to about 1.5, or about 1; then iron can be precipitated at a pH of at least about 9.5, 10, 10.5, 11, 11.5; then aluminum can be precipitated at a pH of about 7 to about 11, about 7.5 to about 10.5, or about 8 to about 9.

**[0078]** The leaching can be carried out under pressure into an autoclave. For example, it can be carried out at a pressure of 5 KPa to about 850 KPa, 50 KPa to about 800 KPa, 100 KPa to about 750 KPa, 150 KPa to about 700 KPa, 200 KPa to about 600 KPa, or 250 KPa to about 500 KPa. The leaching can be carried out at a temperature of at least 80 °C, at least 90 °C, or about 100 °C to about 110 °C. In certain cases it can be done at higher temperatures so as to increase extraction yields in certain ores.

**[0079]** For example, the methods can further comprise precipitating the aluminum ions from the liquid phase by adjusting the pH at a value of about 7 to about 11 or about 8 to about 10.5. The methods can further comprise adding a precipitating agent effective for facilitating precipitation of the aluminum ions. For example, the precipitating agent can be a polymer. For example, the precipitating agent can be an acrylamide polymer.

**[0080]** For example, the seeding agent can be hematite.

### **Example 1**

#### **Preparation of hematite**

**[0081]** Hematite (0.5 g) was added to a basic aqueous composition (300 mL) having a temperature of about 90 °C. The basic aqueous composition contained about 17 to about 20 wt% of iron precipitate under the form of  $\text{Fe}(\text{OH})_2$  and  $\text{Fe}(\text{OH})_3$ . The basic aqueous composition was heated over a period of time of about 5 minutes to about 20 hours under agitation at atmospheric pressure. Hematite was added over a period of time of about 5 minutes to about 20 hours at atmospheric pressure. After about 1 hour, a change of color of the precipitate is observed (from brown to red brick). The red color was intensified until a red intense color having the same color than hematite was obtained.

**[0082]** The above-mentioned example was carried out as a proof of concept. Then further examples have been carried out so as to carry out the precipitation of hematite from a basic aqueous that was derived from an acid leaching solution. The acid leaching solution was obtained by leaching an aluminum-containing ore (for example argillite) with HCl.

### **Example 2**

#### **Preparation of hematite from an aluminum-containing ore sample**



**[0083]** The aluminum-containing ore (for example argillite) can be activated mechanically by grinding. Mineral activation leads to a positive influence on the leaching reaction kinetics. For example, a ball mill can be used in air atmosphere for about 2 to 4 hours. Argillite can be also calcinated. This stage of pretreatment can be accomplished at a calcinating temperature between about 400 to about 700°C for a period about 1 to about 2 hours. These two operations, for example, increase the quantity of extracted aluminum by about 25 to 40%.

### **Acid leaching**

**[0084]** Acid leaching can be made by mixing activated argillite with an acid solution (for example HCl) at elevated temperature and under pressure during a given period of time. For example, the argillite / acid ratio can be of about of 1:3 (weight / volume), the concentration of about 6M, the pressure can be of about 70 to about 80 psi, the temperature can be of about 150 to about 170°C, and the reaction time can be about 1 hour to about 7 hours. Under these conditions, over 90% of aluminum and 100% of the iron can be extracted besides the impurities.

**[0085]** At the end of extraction, the solid (not dissolved portion) can be separated from the liquid rich aluminum and iron by decantation or by filtration, after which is washed. This solid represent about 50 to about 60% of the initial mass of argillite. It can be valorized and be used as constituent alloy.

### **Removal of iron**

**[0086]** The iron contained in the solution can be removed by selectively precipitating it at certain pH values. For example, iron removal can be carried out by precipitation in basic medium at a pH greater than about 11.2. This stage can be made by adding the solution containing aluminum and iron in a basic aqueous composition, for example NaOH at a concentration of 6M.

Other bases such as KOH can also be used. Iron can thus be precipitated under the form of compounds such as  $\text{Fe}(\text{OH})_2$  and/or  $\text{Fe}(\text{OH})_3$ .

**[0087]** During the second half of such a treatment, hematite can be added (can be called seeding hematite). Hematite seed addition can enhance hematite precipitation reaction (for example transformation of  $\text{Fe}(\text{OH})_2$  and/or  $\text{Fe}(\text{OH})_3$  into hematite). For example, 10 g of hematite can be added to 1L of basic aqueous composition optionally under agitation. The concentration of Fe in the solution was about 2.5 to about 3.0 g/L. The reaction temperature can be of about 80°C to about 140°C (for example, the basic aqueous composition can be at such a temperature), and the reaction time can be of about 3 hours to about 72 hours. Under such conditions, about 98% to about 100% of iron can be precipitated and about 70% to 100% of this iron can be precipitated as hematite. Optionally, it is possible to recover iron by using a refining step by liquid-liquid extraction through a hollow fiber membrane.

**[0088]** It is possible 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 1M to 2M). At the end of this step, the solid can be washed with water.

#### **Aluminum recovery**

**[0089]** This step can also be carried in various ways. Aluminum ions can be precipitated under the form of aluminum hydroxide. For example, an hydrated form of  $\text{Al}(\text{OH})_3$  can be obtained by addition of a liquid acid, at a pH of about 7 to about 10.5 or about 7.5 to about 10 or about 9, the temperature can be of about 50°C to about 80°C, and the reaction time can be of about 3 hours to about 24 hours. This step can be made by adding a solution of HCl, for example at a concentration of 6M. Other acid can also be used. From the previous step, for example 90 to 100% aluminum hydroxide can be precipitated.

**[0090]** Alternatively, aluminum ions can be precipitated by addition of an acid gas. For example, an hydrated form of  $\text{Al}(\text{OH})_3$  sprayed by  $\text{CO}_2$ , at a pH of about 7 to about 10.5, the temperature can be of  $50^\circ\text{C}$  to  $80^\circ\text{C}$ , and the reaction time can be of about 3 hours to about 24 hours. From the previous step, for example 90 to 100% aluminum hydroxide can be precipitated.

**[0091]** Another way of precipitating aluminum ions can be carried out by addition of flocculating agent. Various flocculating agents can help to the formation of voluminous flakes which settles by sedimentation. For example, an acrylamide polymer can be used, at a concentration of about 0.1% to about 0.3%. The ratio flocculating agent / solution of hydroxide aluminum can be about 1:300 (volume / volume). The temperature can be below  $30^\circ\text{C}$  and the reaction time can be of about 5 minutes to about 20 minutes. Under such conditions, more about 97% of the aluminum can be precipitated.

### **Example 3**

#### **Preparation of hematite from an aluminum-containing ore sample**

##### **Argillite**

**[0092]** The argillite was ground up in the wet phase in a ball grinder. The mixture of water and roughly crushed argillite coming from the mine was fed into the grinder, where the mineral is reduced to less than 100 microns. The mud went down by gravity into a mixer outfitted with two impellers, which ensures a good homogeneity. When the mixture reaches the desired density, the contents of the mixer are pumped to an accumulation bunker, which will serve to feed the mud to an autoclave.

##### **Acid**

**[0093]** The acid fed to the leaching came from two sources. The major portion was recycled spent acid. This recycled acid contained about 20 to about 22 wt. % of hydrochloric acid ( $\text{HCl}$ ) and about 10 to about 11% of  $\text{AlCl}_3$ .



For example, if excess acid is required, a small quantity of fresh 36 % acid can be used.

### **Leaching**

[0094] The mud of argillite and acid were fed to the autoclave of 32 m<sup>3</sup> in stoichiometric proportion. The autoclave was then hermetically sealed, mixed well and heated by indirect contact with the steam-fed jacket. As the temperature was rising, the steam pressure increased such that the reaction reached a temperature of about 175 °C and a pressure of about 7.5 barg. At the end of the leaching cycle, the metals contained in the argillite were converted into chlorides. The mixture was then cooled by indirect contact with the cooling water in the reactor jacket. When the mixture was at about 70 to about 80 °C, the leached mud was transferred by air pressure to two buffer reservoirs maintained in communicating vessels for further treatment and disposal and the leachate was thus ready for further treatments.

### **Preparation of hematite**

[0095] The mother liquor from leaching (leachate) was pumped at constant rate across cartridge filters to the first iron precipitation reactor. This reservoir was well mixed and the temperature was controlled to about 65 to 70 ° C by means of a heating coil. The pH was continuously metered and the solution was maintained at a pH of about 12 by addition of 50 wt % caustic soda with the help of a dispensing pump. The precipitation reaction converted the iron chloride and the other metal chlorides into hydroxides, which were leading to a gradual precipitation and agglomeration of the solid crystals. The leachate was then fed consecutively to two other precipitation reactors when the pH was also controlled by the addition of caustic soda and the temperature maintained by a heating coil. At the exit from the last reactor, the liquor was fed to a gravity decanter.

### **Decanting and seeding**

[0096] The purpose of the gravity decanter was to produce a thickened mud of the largest crystals of hematite. These crystals served for the seeding

in the first precipitation reactor. It was observed that such a technique was useful to promote the creation of precipitates (hematite) that are larger and more easy to filter. A quantity of about 1.5 to about 5.5 g of hematite per liter of the solution was used for seeding. The concentration of Fe in the solution was about 2.5 to about 3.0 g/L.

#### **Filtration of hematite**

[0097] The filtration of the hematite was carried out with the help of two automated filter presses. The mother liquor was then sent to a buffer reservoir to be pumped to the aluminum precipitation reactor.

#### **Neutralization of hematite**

[0098] The washed hematite was sent to a blade mixer where the pH of the solid is metered. A pH less than about 8 was maintained by the addition of hydrochloric acid (HCl) with the help of a dispensing pump..

#### **Precipitation of aluminum**

[0099] For the precipitation of the aluminum, the pH of the mother liquor was adjusted to about 9.5 by reacting it with HCl. Since the mother liquor has been controlled at 65° C with the help of a heating coil. The pH was metered continuously and the solution was maintained at pH of about 9.5 by addition of HCl using a dispensing pump. The precipitation reaction was effective for converting the aluminum chloride into aluminum hydroxide, which resulted in a gradual precipitation and agglomeration of solid crystals. The liquor was then sent consecutively to two other precipitation reactors where the pH was also controlled by the adding of acid and the temperature maintained by a coil. At the exit from the last reactor, the liquor is fed to a gravity decanter.

#### **Decanting and seeding**

[00100] A gravity decanter was also used to produce a thickened  $\text{Al}(\text{OH})_3$  mud of the largest crystals. These crystals were pumped from the bottom of the decanter to the first precipitation reactor to seed the crystallization.

[00101] The rest of the  $\text{Al}(\text{OH})_3$  mud and the supernatant fluid of the decanter were sent to a repulping tank from which the mixture was pumped to a centrifuge type separator/washer. After the treatment with the separator, the  $\text{Al}(\text{OH})_3$  was then dried.

[00102] The scope of the claims should not be limited by specific embodiments and examples provided in the disclosure, but should be given the broadest interpretation consistent with the disclosure as a whole.



**WHAT IS CLAIMED IS:**

1. A method for preparing hematite, said method comprising obtaining said hematite from a basic aqueous composition comprising at least one precipitated iron ion, having a pH of about 10.5 to about 13 and being at temperature of about 50 °C to about 150 °C, by reacting said composition with a predetermined quantity of hematite in the absence of a growth regulating agent, thereby promoting, catalyzing and/or enhancing formation of said hematite, wherein said basic aqueous composition is obtained by :

leaching an iron-containing material comprising said at least one iron ion with an acid so as to obtain a leachate and a solid residue;

separating said leachate from said solid residue; and

reacting said leachate with a base

or by :

leaching said iron-containing material comprising said at least one iron ion with an acid so as to obtain a leachate and a solid residue;

optionally removing at least a portion of said at least one iron ion from said leachate;

separating said leachate from said solid residue; and

reacting said leachate with a base.

2. The method of claim 1, wherein said at least one precipitated iron ion is  $\text{Fe}^{3+}$ .
3. The method of claim 1, wherein said at least one precipitated iron ion is  $\text{Fe}^{2+}$ .
4. The method of claim 1, wherein said at least one precipitated iron ion is chosen from  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$ , and a mixture thereof.
5. The method of claim 1, wherein said at least one precipitated iron ion is under the form of  $\text{Fe}(\text{OH})_3$ .
6. The method of claim 1, wherein said at least one precipitated iron ion is under the form of  $\text{Fe}(\text{OH})_2$ .

7. The method of claim 1, wherein said at least one precipitated iron ion is under the form of  $\text{Fe}(\text{OH})_2$ ,  $\text{Fe}(\text{OH})_3$ , or a mixture thereof.
8. The method of any one of claims 1 to 7, wherein said predetermined quantity of hematite is added to said composition, over a predetermined period of time, under agitation.
9. The method of any one of claims 1 to 8, wherein said basic aqueous composition has a temperature of about 50 °C to about 70 °C.
10. The method of any one of claims 1 to 8, wherein said basic aqueous composition has a temperature of about 75 °C to about 110 °C.
11. The method of any one of claims 1 to 8, wherein said basic aqueous composition has a temperature of about 80 °C to about 100 °C.
12. The method of any one of claims 1 to 8, wherein said basic aqueous composition has a temperature of about 85 °C to about 95 °C.
13. The method of any one of claims 1 to 8, wherein said basic aqueous composition has a temperature of about 87 °C to about 93 °C.
14. The method of any one of claims 1 to 8, wherein said basic aqueous composition has a temperature of about 70 °C to about 120 °C.
15. The method of any one of claims 1 to 14, wherein said basic aqueous composition has a pH of about 10.8 to about 11.8.
16. The method of any one of claims 1 to 14, wherein said basic aqueous composition has a pH of about 11.0 to about 11.6.
17. The method of any one of claims 1 to 14, wherein said basic aqueous composition has a pH of about 11.2 to about 11.5.
18. The method of any one of claims 1 to 14, wherein said basic aqueous composition has a pH of about 10.5 to about 12.
19. The method of any one of claims 1 to 14, wherein said basic aqueous composition has a pH of about 11.5 to about 12.5.

20. The method of any one of claims 1 to 14, wherein said basic aqueous composition has a pH of about 11.8 to about 12.2.
21. The method of any one of claims 1 to 20, wherein said basic aqueous composition is maintained at said pH when being reacted with said hematite.
22. The method of any one of claims 1 to 21, wherein said basic aqueous composition is maintained at said temperature when being reacted with said hematite.
23. The method of any one of claims 1 to 22, wherein said predetermined quantity of hematite is added at a molar ratio hematite / said at least one iron ion of about 0.005 to about 0.5.
24. The method of any one of claims 1 to 22, wherein said predetermined quantity of hematite is added at a molar ratio hematite / said at least one iron ion of about 0.01 to about 0.1.
25. The method of any one of claims 1 to 24, wherein said iron-containing material is chosen from argillite, red mud, fly ashes and mixtures thereof.
26. The method of any one of claims 1 to 24, wherein said iron-containing material is argillite.
27. The method of any one of claims 1 to 26, wherein said base is NaOH.
28. The method of any one of claims 1 to 26, wherein said base is KOH.
29. The method of any one of claims 1 to 28, wherein said base has a concentration of about 2 to about 20 M.
30. The method of any one of claims 1 to 28, wherein said base has a concentration of about 3 to about 4 M.
31. The method of any one of claims 1 to 28, wherein said base has a concentration of about 30 to about 60 weight %.
32. The method of any one of claims 1 to 28, wherein said base has a concentration of about 35 to about 55 weight %.



33. The method of any one of claims 1 to 28, wherein said leachate and a first portion of said base are added simultaneously into a reactor comprising a second portion of said base.
34. The method of any one of claims 1 to 33, wherein said hematite is recovered by means of a gravity decanter.
35. The method of any one of claims 1 to 34, wherein said basic aqueous composition is obtained by :

leaching said iron-containing material comprising said at least one iron ion with an acid so as to obtain a leachate and a solid residue;

separating said leachate from said solid residue; and

reacting said leachate with said base.

36. The method of any one of claims 1 to 34, wherein said basic aqueous composition is obtained by :

leaching said iron-containing material comprising said at least one iron ion with said acid so as to obtain a leachate and a solid residue;

optionally removing at least a portion of said at least one iron ion from said leachate;

separating said leachate from said solid residue; and

reacting said leachate with a base.

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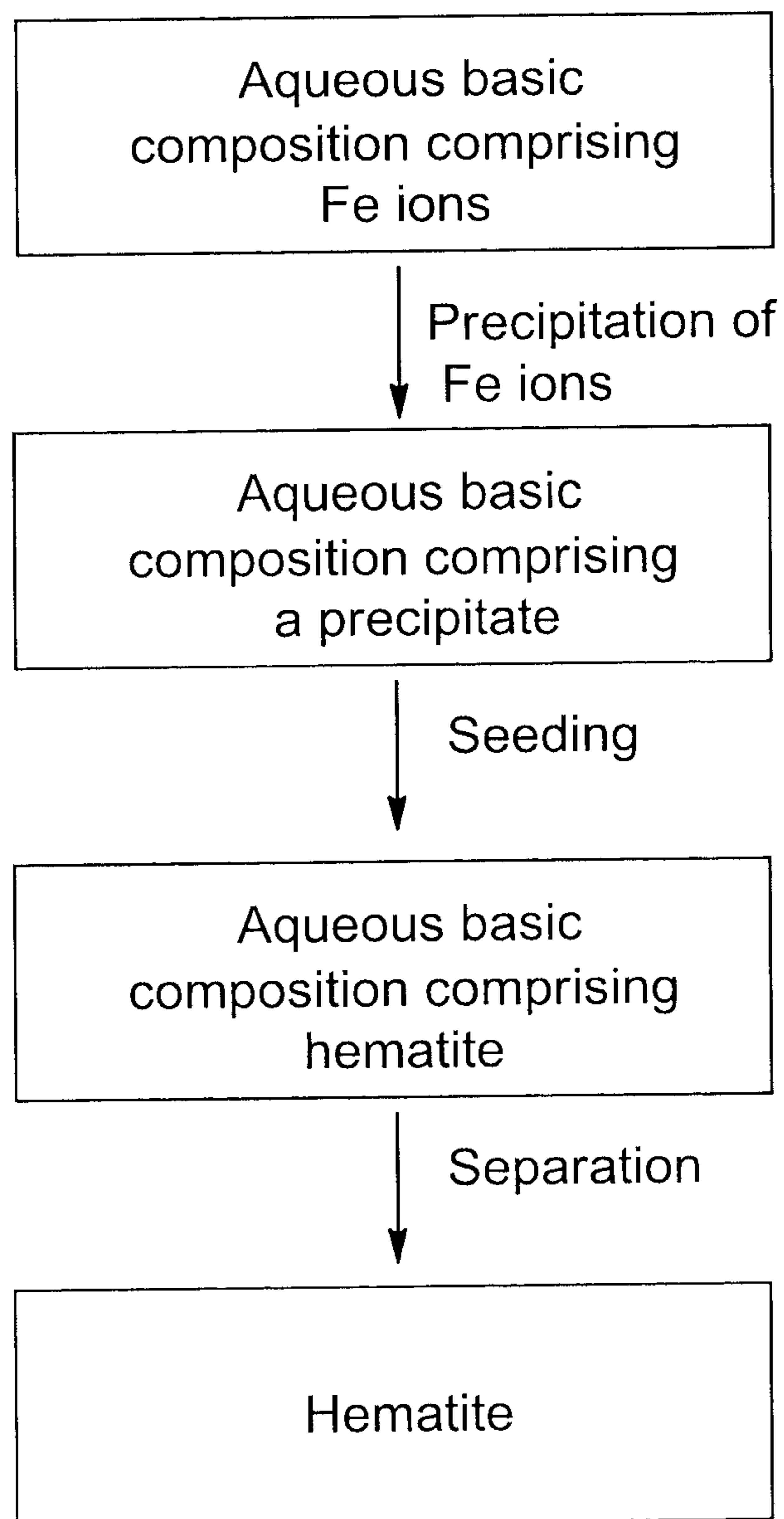


FIG. 1

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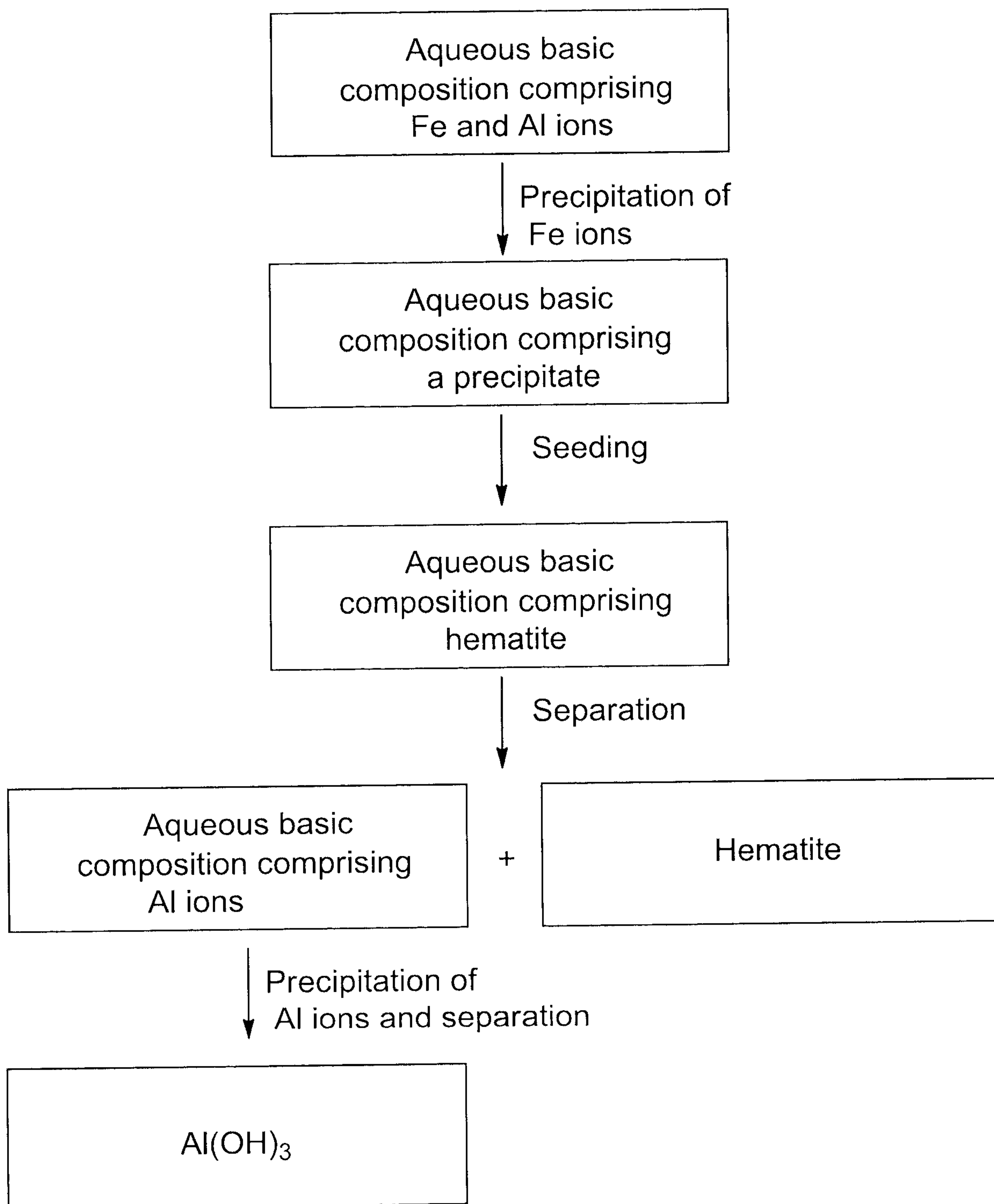


FIG. 2