Method for energy-economic exploitation of aluminium containing rocks and minerals

Abstract: Method for energy-economic utilization of aluminium containing rocks and mineral for manufacture and isolation of valuable minerals. The aluminium containing rocks are in a first process step comminuted and dissolved in a mixture of CO2 and water under pressure at a pH in the range 3-7 and a temperature of about 300 °C and a pressure in the range 1-150 bar, the aluminium hydroxide thereby being directly precipitated and separated from the solution together with any compounds of iron and magnesium as well as any undissolved material. Reaction products in solution comprising both SiO2 and CaCO3 ions are continuously removed from the first process step while additional CO2 and H2O are continuously added so that the reaction takes place in absence of equilibrium. SiO2 and CaCO3 are precipitated in subsequent process step at a pH higher than in the first process step.
METHOD FOR ENERGY-ECONOMICAL
EXPLOITATION OF ALUMINIUM CONTAINING
ROCKS AND MINERALS

The present invention concerns a method of manufacturing aluminium containing raw
material/intermediate products combined with production of precipitated silica, from
aluminium containing rocks in an energy-economic process. At the same time
immobilizing of CO₂ is achieved with a corresponding benefit in the form of reduced risk
of greenhouse effect.

Background

Globally there is a substantial need for exploitation of naturally occurring resources in the
form of minerals. The need is increasing not least due to increased industrialization in
countries formerly known as developing countries and which is about to develop into
industrialized countries with regard to production, consumption and infrastructure. It is
of major importance both economically and with respect to the climate that exploitation
and refining of minerals can take place in processes that are as energy economical as at all
possible and which to the smallest possible degree increases the burdens on the
environment locally and globally.

It should be noted that anthropogenic emission of CO₂ is one of the largest environmental
challenges of our time.

CO₂ may e.g. be bound to CaO under precipitation of CaCO₃. This reaction implies that
CO₂ produced in industrial processes, like in gas power plants and during hydrogen
production based on natural gas, can be immobilized.

Manufacture of CaO from CaCu₃ (limestone, the most common CaO source) is though not
interesting in a climate perspective since the production of CaO in this connection leads to
formation of the same amount as can later be bound, therefore the net effect is zero.

With regard to the manufacture of CaO or Ca²⁺ ions from sources other than carbonates,
such as silicates, sulphates, and phosphates, the situation is different. Most of the calcium
including silicate (and phosphate) minerals available in sufficient amounts do, however,
not seem to represent a basis for an economically feasible manufacture of CaO or Ca²⁺
ions unless the mineral or the rock has one or more additional elements that also may be
exploited commercially. One example of a useful rock is the silicate rock anorthosite,
which in addition to be a source for Ca²⁺ and production of the end product CaCO₃ (also
denoted precipitated calcium carbonate (PCC)), also may be used as raw material for
aluminium production in combination with production of precipitated silica (SiO₂).
The rock anorthosite, which is present in large amounts e.g. in the Sognefjorden (Norway) area, comprises mainly the minerals anorthite (CaAl₂Si₂O₈) and some albite (NaAl₃SiO₈) and contains about 15 %CaO. Anorthosite is through established acidic processes (e.g. the Anorthal process including HCl and a nitric acid/ammonia process, Norwegian patent No. 302864) a raw material of interest for the aluminium industry.

In the nature the following reaction:

\[
\text{CO}_2 + 2\text{H}_2\text{O} + \text{CaAl}_2\text{Si}_2\text{O}_8 \rightarrow \text{Al}_2\text{Si}_2(\text{OH})_4 + \text{CaCO}_3
\]

(Anorthosite) (kaoline) (limestone)

occurs very slowly due to that, after all, in this connection there are small amounts of CO₂ in the atmosphere (350 ppm) and the temperature is low, at least at northern latitudes. The reaction rate may, however, be increased under process conditions and be optimized by varying pressure, temperature and the amount ratios of CO₂ to H₂O. The fine grain mixture of the reaction products obtained, kaolin and limestone (CaCO₃) can then be used directly in the so-called Lime Sinter Process, also denoted Ancor Process (J. H. Reimers, 1947: Aluminium, Tanum 1947, s. 24, and patent nr. 302863).

In the Ancor Process kaolin (Al₂Si₂(OH)₄) is the aluminium raw material. This process has an energy demanding sintering step. In the preferred embodiment in (Norwegian) patent No. 302 863 (fig. 2 in the patent) the energy demanding sintering step is avoided since kaolin is not formed. The aluminium of the anorthosite is in stead converted to aluminium hydroxide illustrated by the simplified reaction equation shown below:

\[
\text{CaAl}_2\text{Si}_2\text{O}_8 + \text{CO}_2 + 3\text{H}_2\text{O} \rightarrow 2\text{Al(OH)}_3 + \text{CaCO}_3 + 2\text{SiO}_2
\]

In the preferred embodiment in 302 863 the silicon and calcium from the anorthosite is filtered out as 2H₄SiO₄/CaCO₃ (fig. 2 of the patent) without further preparation or separation for product manufacture.

Objectives

It is an object of the present invention to provide a process for the manufacture of aluminium containing raw material or intermediate product suitable for further refining to
aluminium containing products based on aluminium containing rocks in a manner which is economically efficient and sustainable. In the last aspect is understood that the method shall not incriminate the surrounding environment significantly with greenhouse gases or pollution.

It is furthermore an object to combine the manufacture of an aluminium raw material with the production of precipitated silica.

It is a further object of the invention to provide a method as defined above at which free CO2 may be immobilized to thereby reduce the incrimination of the environment in the form of greenhouse gases and greenhouse effect.

The present invention

The objects mentioned above are fulfilled by the present invention as defined by claim 1.

Preferred embodiments of the invention are disclosed by the dependent claims.

According to the present invention CO2 from a combustion plant or other CO2 source, like a power plant burning fossil fuel (or bio fuels) is combined with the manufacture of aluminium raw material in a process plant, the raw material thereafter being converted to alumina (Al2O3) for the production of aluminium. At the same time other minerals can be taken care of and refined. The method may for instance include also the manufacture of precipitated silica (SiO2) and possibly also precipitated calcium-magnesium-carbonate (PCC, CaCO3) from the same rocks. Another option is that also raw material for production of iron, titanium and zirconium is handled in a continuous process based for instance, though not exclusively, on the rocks anorthosite (mainly comprising the minerals anorthite (CaAl2SiO8) and some albite (NaAl3SiO8)), other feldspar and feldsparoid rich rocks as well as alkaline and ultra-alkaline rocks and their metamorphous equivalents.

Due to i.a. maintained lack of equilibrium in the dissolution reactor it has been shown possible to dissolve industrially these aluminium containing rocks under such mild conditions as here described with regard to temperature and pH. In this way an expensive and energy demanding heating process to a higher temperature is avoided as is also the use of strong mineral acids which would have introduced undesired ions like chloride, nitrate or sulphate into the process.
In the following the invention is exemplified in more details through a discussion of the rock anorthosite.

In this embodiment of the invention comminuted anorthosite is brought to react with CO2 and H2O (carbonic acid) in a dissolution reactor. In the dissolution reactor aluminium hydroxide is precipitated as is iron and magnesium hydroxides, which mostly originates form the anorthosite’s remaining content of dark minerals (after magnetic separation or other enrichment processes). "Dark minerals" refers to minerals comprising mostly iron, magnesium, aluminium and silicon, with or without water, pyroxenes, amphibolites, or combinations of said materials.

Different from the process described in Norwegian patent 302 863, in the present invention silicon oxide (SiO2) and calcium in the form of calcium ions (Ca2+) are brought out of the dissolution reactor in solution for separation in separate precipitation reactors for the manufacture of calcium carbonate (CaCO3) and amorphous silicon oxide (SiO2). Another difference from the process of NO patent 302 863, no mineral acid such as HCl, possibly in connection with CO2 and H2O is used to optimize the pH in the present reaction between the rock and CO2 and water. A mineral acid would introduce chloride, nitrate or sulphate ions which would create an extra complexity of the subsequent process and represent a procedural "pollution problem" that is undesired and cost increasing.

In the preferred embodiment of the present invention the amount ratio between H2O and CO2 is used in addition to changing the pressure and temperature to reach a desired pH for dissolution of the rock and for precipitation of the calcium carbonate and SiO2 in separate precipitation reactors.

As an option organic acids may be added together with CO2 and H2O in order to reach optimal pH for procedural conditions, especially during the dissolution step of the rock.

The advantage of using organic acids characterized by the carboxyl ion COO⁻ as compared to mineral acids, is that the organic acid can be degraded under heating to just CO2. The inherent disadvantages of the mineral acid anions Cl⁻, SO₄²⁻, and NO₃⁻ can this way be avoided. Organic acids can optionally be used if it is in the production process is desirable with a lower pH than what is achievable by use of just CO2 and H2O (a pH of about 3).
Embodiments of the present invention with different variants based on different rocks as a basis, will now be described in further detail with reference to the accompanying drawings, where:

Fig. 1 is a schematic view of exemplified utilization of the rock anorthosite in which sodium carbonate containing water is released (area inside the broken line represents the invention).

Fig. 2 shows an embodiment of the present invention in which sodium carbonate with natural sodium from the rock is used to dissolve aluminium from the hydroxide composition (area inside the broken line represents the invention).

Fig. 3 is a schematic view of an embodiment with a more general utilization of feldspar rich and feldsparoid rocks, as well as alkaline rocks and ultra-alkaline rocks (rocks without free or with little quartz (SiO2)) and their metamorphous equivalents (area inside the broken line represents the invention).

Fig. 1 shows how CO2 and water is combined to obtain an optimal pH 3-5, by typically using a pressure in the range 1-200 bars, more preferred 20-170 bars and most preferred in the range 50-150 bars, prior to introduction in the dissolution reactor Rl. In the same step of combination (of CO2 and H2O) the temperature is preferably in the range 50-220 °C, more preferred in the range 100-170 °C.

In the present invention no mineral acid (such as HCl, HNO3, H2SO4) is used to reduce the pH to a level lower than what is possible with just CO2 and water. In the present invention only CO2 and water is used in varying amounts and with varying pressure and temperature. Optionally an organic acid can be added to reach a pH lower than 3, e.g. in the range 1-3, to increase the rate of dissolution of the rock (anorthosite) in the dissolution reactor Rl, if so desired. Addition of an organic acid does not introduce ions that can create problems and lead to cost increase later in the process (separation, recovery, pollution etc.) Organic acids may as mentioned be degraded to CO2 and be recycled to the step of combination of CO2 and H2O to be introduced in the dissolution reactor Rl.
A difference from Norwegian patent No. 302863, in which $2H_4Si(VCaCO_3$ is filtered out as a solid substance, $SiO_{2(aq)}$ and the ions $Ca^+, Na^+$ and $CO_3^{2-}$ are, according to the present invention, brought out of the dissolution reactor $R1$ in solution, together with carbonic acid ($CO_2 + H_2O$) into $R2$ (the second process step) for precipitation of calcium carbonate ($CaCO_3$).

Solids precipitation in $R1$, mostly in the form of aluminium hydroxide, possibly contaminated by iron and magnesium hydroxide, as well as undissolved components of the original rock, are brought out of the dissolution reactor for further processing (see $RS2$ and Fig. 2), or for sale as an aluminium raw material (can be described as a high quality bauxite). If the iron and magnesium source from dark minerals (e.g. amphibol, klino and orthopyroxene) may effectively be removed in the enrichment process for the anorthosite (like magnetic separation, flotation etc.) the aluminium raw material in $R1si$ may be directly calcinated to the end product alumina, $Al_2O_3$.

In the second process step ($R2$) where the end product precipitated calcium carbonate ($CaCO_3$) is precipitated, $pH$ is always higher than in the first process step ($R1$) and preferably in the range 5-13. The pressure in second reactor is typically in the range 1-150 bars, more preferred 20-130 bars and most preferred 50-80 bars. In the same step the temperature is preferably in the range 100-300 °C, more preferred in the range 140-250 °C.

There are different ways to separate the different process steps, but in a continuous process or a process in which the object is to separate Al raw material from precipitated calcium carbonate and from precipitated silica, it is required to use separate reactors or separate reactor chambers for the different process steps, so that substantially stationary conditions may be maintained in each separate reactor or each separate reactor chamber. Thus the first process step, dissolution of the rock, takes place in a first reactor chamber $R1$, while precipitation takes place in another reactor chamber $R2$, which only receives liquid material from the first reactor chamber (the dissolution reactor $R1$), whereas precipitated aluminium hydroxide (possibly along with precipitated bi-products, Fe and Mg hydroxides, etc.) and any undissolved rock, is separated out to ($R1si$).

As already mentioned the pressure is preferably reduced from first reactor chamber $R1$ to second reactor chamber $R2$, so that some $CO_2$ is thereby released from the solution and the solution $pH$ thereby correspondingly increased. It should be noted that according to
this invention no further chemicals are added (such as NaOH or NH₃) to increase pH. Furthermore the temperature is preferably increased from first to second reactor chamber to thereby favour precipitation of CaCO₃.

Precipitation of amorphous silica takes place in a third reactor chamber R₃ which solely receives liquid material (SiO₂ + Na⁺ + CO₃²⁻ + H₂O) from the second reactor chamber R₂. Precipitation of amorphous silica thus takes place in a third process step R₃, typically at a lower temperature (0-200 °C) and a lower pressure (1-50 bars) than process step 2.

The process is typically conducted as a continuous process with respect to the liquid flow through the process and more preferred the entire process is conducted as a continuous process.

It should be emphasized that the method according to the invention also is useful because it allows an industrial manufacture or isolation of valuable mineral compounds combined with immobilization of used CO₂.

After separation of amorphous silica, an aqueous solution comprising sodium ions (Na⁺) and an amount of carbonate ions (CO₃²⁻) equivalent to the amount of sodium ions, is also immobilized.

Some of the anorthosite’s natural content of sodium (Na₂O, 2-6%) may, however be used to produce a solution of sodium aluminate (NaAlO₂) from the precipitated product (mainly Al hydroxide in R₁ and R₁s₂) which in turn is treated further in a production plant like a variant of the known Bayer process, for formation of Al₂O₃, see fig. 2 of the enclosed drawings. As an option natural Na⁺ and CO₃²⁻ from the process may be added to sodium carbonate and/or sodium hydroxide to optimize the solution of aluminium hydroxide as sodium aluminate (see fig. 2).

Fig. 3 shows how CO₂ and water is combined to obtain an optimal pH 3.5 by typically using a pressure in the range 1-200 bars, more preferred 20-170 bars and most preferred in the range 50-150 bars before being introduced in the dissolution reactor R₁, which in this case contains a or mixtures of a number of feldspar rich and/or feldspathoid rocks (± 90 % feldspar) comprised substantially by a) plagioclase series (anorthite CaAl₂Si₂O₈ and albite NaAlSi₃O₈), b) ± kalifeldspars (K(Na)(AlSi₃O₈)) and c) ± the feldspathoids represented by the nepheline group (KNa(AlSiO₄)) and so-called alkaline and ultra-alkaline rocks (gabbros) without free quartz, (SiO₂) with the significant minerals in addition to the before...
mentioned pyroxene group (Ca, Na, Li) (Mg, Fe, Al, Ti) [(Si, Al)2O6] ± the amphibole group 
(chemically equal to the pyroxene group, with addition of OH groups or water) and these 
rocks metamorphous equivalents (eclogites, garnet-amphibolite, garnet peridotite with 
the minerals pyroxene (omphacite (Na, Ca)(Al, Mg, Fe) (Si2O6) ± amphibole ± olivine).

In the formulas above elements separated by a comma within a parenthesis is to be 
understood as at least one of these elements being present and in practice typically at 
least two of the indicated elements will be present in an unspecified amount ratio. It is 
certainly not a requirement that all elements separated by comma shall be simultaneously 
present in a defined rock or mineral even though this situation commonly occurs.

In the combination step (at the dissolution reactor Rl) the temperature is preferably 50-
220 °C, but more preferred in the range 100-170 °C.

In the present invention mineral acid (e.g. HCl, HNO3, H2SO4) is not used to reduce pH. 
Preferably only CO2 and water is used for pH adjustments in combination with 
adjustments of pressure. As an option an organic acid (e.g. formic acid, acetic acid) can be 
used to reach a pH lower than about 3, e.g. in the range 1-3, in order to, if desired, to 
increase the dissolution rate of the rock in question in the dissolution reactor Rl.

Utilization of an organic acid does not imply introduction of ions from mineral acids which 
would cause problems later in the process (separation, recovery/contamination, etc.) 
because the organic acids can be degraded to just CO2 and H2O in the further process and 
be recycled to the combinations step of CO2 and H2O to be introduced in the dissolution 
reactor Rl.

The solids precipitation in Rl, comprising varying amounts between aluminium hydroxide 
and iron hydroxide as well as undissolved material from the originating rock, e.g. ± 
zirconium, ± rutile, ± magnetite, ± ilmenite, ± other, dependent on the originating rock, are 
brought out of the dissolution reactor Rl for further processing, Rls. For all feldspar rich 
and feldspathoid rocks the aluminium hydroxide will dominate completely, while for 
alkaline rocks iron hydroxide (in oxidated state) may dominate. Some magnesium and 
calcium will in this process step be able to precipitate along with aluminium and iron. The 
remaining part of the rock's original content of calcium and magnesium will follow the 
solution as ions Ca2+ and Mg2+, along with SiO2− (aq), CO32− and alkali metal ions (Na+, K+, 
Li+, Cs+, and Rb+) to R2 (fig. 3).
In the second process step (R2) where calcium-magnesium carbonate (or a combination carbonate between calcium and magnesium) is precipitated, pH is always higher than in first process step Rl and preferably in the range 5-13. The pressure in second reactor R2 is typically in the range 1-150 bars, more preferred 20-130 bars and most preferred 50-80 bars. In the same step the temperature preferably is in the range 100-300 °C, more preferred in the range 140-250 °C.

There are different methods to separate the different process steps from one another, but in a continuous process or in a process in which the object is to separate Al raw material (alternatively Fe raw material) from precipitated calcium (-magnesium) carbonate from precipitated silica, it is necessary to utilize separate reactors or separate reactor chambers for the different steps so that substantially constant conditions may be maintained in each reactor or each reactor chamber. Thus, the first process step, the dissolution step, takes place in a first reactor chamber (Rl) while precipitation of calcium (-magnesium) carbonate takes place in another reactor chamber, R2, that solely receives fluent material from the first reactor chamber (the dissolution reactor Rl), while precipitated aluminium hydroxide/iron hydroxide and any undissolved rock are separated out (Rls).

As already mentioned the pressure is preferably reduced from first reactor Rl chamber to second reactor chamber R2 so that some CO₂ thereby leaves the solution and the pH is correspondingly increased. No extra additives (like NaOH, NH₃) are used to adjust the pH. Furthermore the temperature is preferably increased from first to second reactor chamber to thereby favour precipitation of calcium (-magnesium) carbonate.

Precipitation of amorphous silica typically takes place in a third reactor chamber R3 that solely receives fluent material (SiO₂(αq) and alkaline metal ions + CO₃²⁻ + H₂O) from second reactor chamber (R2). Precipitation of amorphous silica takes place in a third process step (R3). This typically is conducted at lower temperature (0-200 °C) and lower pressure (1-50 bars) than process step 2. The process is typically conducted as a continuous process with respect to the liquid flow through the process and more preferably the entire process is conducted as a continuous process.

It should be emphasized that the method according to the invention is particularly useful because it combines industrial production of valuable minerals and raw materials with immobilization of CO₂.
After separation of amorphous silica combined with partial evaporation, an aqueous solution comprising alkaline metal ions and carbonate ions (CO\(_3^{2-}\)) is released or lodged in the ocean. Possibly specific alkaline metal ions may be separated out and used.

It is important to note that CO\(_3^{2-}\) in amounts equivalent to the alkali metal ions together with amounts precipitated calcium-magnesium carbonate can give a significant contribution to CO\(_2\) immobilization.

By aluminium containing product is referred to any chemical composition comprising aluminium for any useful purpose, either as an end product for use or sale, an intermediate product to be further refined in any connection what so ever or in other contexts.

Generally any aluminium containing rock or any aluminium containing mineral can be used in the method according to the present invention, but there are some that are not optimal for the process. A person skilled in the art will be able to deduct which minerals are well suited and which are less well suited, either theoretically, empirically or through a combination of theoretic and empiric deductions.

Rocks containing significant amounts of free quartz are less well suited than many other rocks since they to a lesser extent will be dissolved and in stead be part of the process flows as undissolved powder.

In some embodiments it is preferred not to add any acid to the dissolution reactor except CO2. Under any circumstances it is important not to add mineral acids/ inorganic acids to avoid problems related to contamination of the process by anions such as chloride, nitrate, sulphate, etc.

It is not significant in relation to the process whether any used combination of CO2 and water prepared in connection with the process is prepared for the purpose or is added as an already existing aqueous solution of carbonic acid.
Claims:

1. Method for energy economic utilization of aluminium containing rocks and mineral for manufacture and isolation of valuable minerals, characterized in that
   - the aluminium containing rocks are in a first process step comminuted and dissolved in a mixture of CO₂ and water under pressure at a pH in the range 3-7 and a temperature of about 300 °C and a pressure in the range 1-150 bar, the aluminium hydroxide thereby being directly precipitated and separated from the solution together with any compounds of iron and magnesium as well as undissolved material,
   - reaction products in solution comprising both SiO₂ and Ca²⁺ ions are continuously removed from the first process step while additional CO₂ and H₂O are continuously added so that the reaction takes place in absence of equilibrium, while
   - SiO₂ and CaCO₃ are precipitated in subsequent process step at a pH higher than in the first process step.

2. Method as claimed in claim 1, characterized in that pH is raised from first to second process step solely through pressure reduction and that CaCO₃ is precipitated in second process step.

3. Method as claimed in claim 1, characterized in that the method in its entirety is conducted without addition of mineral acids.

4. Method as claimed in claim 1, characterized in that SiO₂ that leaves first process step in solution, is precipitated in a subsequent process step, separately from the precipitation of CaCO₃ and at a lower pressure and temperature than in the second process step.

5. Method as claimed in claim 1, characterized in that other undissolved materials comprise ilmenite, magnetite, zirconium and baddebyite, which are separated from for utilization of iron, titanium and zirconium.

6. Method as claimed in claim 1, characterized in that precipitated aluminium hydroxide is refined to Al₂O₃ in a per se known manner (Bayer process).

7. Method as claimed in claim 1, characterized in that a part of the carbonate ions (CO₃²⁻) leaving first step in solution and second process step in equivalent amounts with alkali metal ions, are released to seawater with no risk of contributing to CO₂ emission.

8. Method as claimed in claim 1, characterized in that the aluminium containing rock is a rock rich in feldspar.
9. Method as claimed in claim 1, characterized in that the aluminium containing rock is anorthosite.

10. Method as claimed in claim 1, characterized in that pH is adjusted in first process step solely by controlled addition of CO₂ and pressure adjustment.

11. Method as claimed in claim 1, characterized in that the reduction of pH in any reaction step in the process solely is conducted through one or more of the following means, addition of CO₂, increase in pressure, addition of organic acid.

12. Method as claimed in claim 1, characterized in that pH in the first process step is in the range 3-5, that the pressure in first process step is in the range 1-200 bar, more preferred in the range 20-170 bar and most preferred in the range 50-150 bar, while the temperature in the first process step is in the range 50-220 °C, more preferred 100-170 °C.

13. Method as claimed in claim 1, characterized in that pH in the second process step is in the range 5-13, that the pressure in second process step is in the range 1-150 bar, more preferred in the range 20-130 bar and most preferred in the range 50-80 bar, while the temperature in second process step is in the range 100-300 °C, more preferred 140.250 °C.

14. Method as claimed in claims 1-13, characterized in that there is a simultaneous production of Al₂O₃ and highly pure SiO₂ in a process in which the highest temperature is at most 300 °C.
Figure 1

Calsination

Al₂O₃

Addition of lye

NaOH

Na₂AlO₂

in solution

Fe, Mg hydroxides

Manuf. of Al₂O₃

R₁ s₁

Al-hydroxides

R₂ s₂

Al-hydroxides + any Fe, Mg

Optional addition of organic acids

R₁ s₁

(Anorthosite)

R₂ s₂

(CaCO₃)

R₃ s

(SiO₂)

CO₂-H₂O

CO₂-H₂O

CO₂

CO₂-H₂O

CO₂-H₂O

Discharge/disposal

Na⁺

CO₃²⁻

H₂O

R1

R2

R3

Na⁺

Ca²⁺

CO₃²⁻

Na⁺

SiO₂

Na⁺

Ca²⁺

CO₃²⁻
Figure 2

CO₂-H₂O

Optional addition of organic acids

R1 (Anorthosite)

CO₂-H₂O
SiO₂
Ca²⁺
CO₃²⁻
Na⁺

R2

CO₂
SiO₂
Na⁺
CO₃²⁻

R3

CO₂-H₂O

CO₂-H₂O

R1 s₂ (Al-hydroxides + any Fe, Mg)

Na⁺, CO₃²⁻, (OH⁻), H₂O

Precipitation of Al(OH)₃

Filtration

Calsination to Al₂O₃

NaAlO₂

R1 s₂ in solution

Na⁺, CO₃²⁻, (OH⁻), H₂O

→ evaporation

Filtration

Fe, Mg hydroxides

(+ optionally added Na₂CO₃ or NaOH for optimal dissolution of Al-hydroxide as sodium aluminate (NaAlO₂))

Discharge/disposal

Na⁺
CO₃²⁻
H₂O
Figure 3

1. Addition of NaOH
2. Manufacture of Al₂O₃ in solution
3. Addition of NaAlO₂
4. Manufacture of Al₂O₃

- R1: Al-hydroxides + any Fe-hydroxides, and undissolved minerals with e.g. Fe, Ti, Zr.
- Other elements as raw material for manufacture of iron or iron alloys, raw material for manufacture of titanium, zirconium, and other elements depending upon contents in original rock.

- R2: Ca(Mg)CO₃
- Alkali metal ions

- R3: (SiO₂)
- Alkali metal ions

- R₂: CaCO₃
- Alkali metal ions

- R₃: SiO₂
- Alkali metal ions

- CO₂·H₂O
- CO₂·H₂O
- CO₂·H₂O

- Optional addition of organic acids

- Discharge, disposal, or optional use of alkali metals
# INTERNATIONAL SEARCH REPORT

**International application No:** PCT/NO2009/000310

## A CLASSIFICATION OF SUBJECT MATTER

**IPC** 9 C01F 7/20, C01F 11/18, C01B 33/187

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

## B HELD SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

**IPC** C01F, C01B

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

SE, DK, FI, SE classes as above

Electronice data base consulted during the International search (name of data base and, where practicable, search terms used)

EPODOC, WPI

## C DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No</th>
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<td>Y, D</td>
<td>NO 302863 B1 (Institutt for energiteknikk) 1995-09-15 (see page 3, line 22-31; figure 2).</td>
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## D Further documents are listed in the continuation of Box C

- '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
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- X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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04/12/2009

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<td>EP 1951622 A1</td>
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