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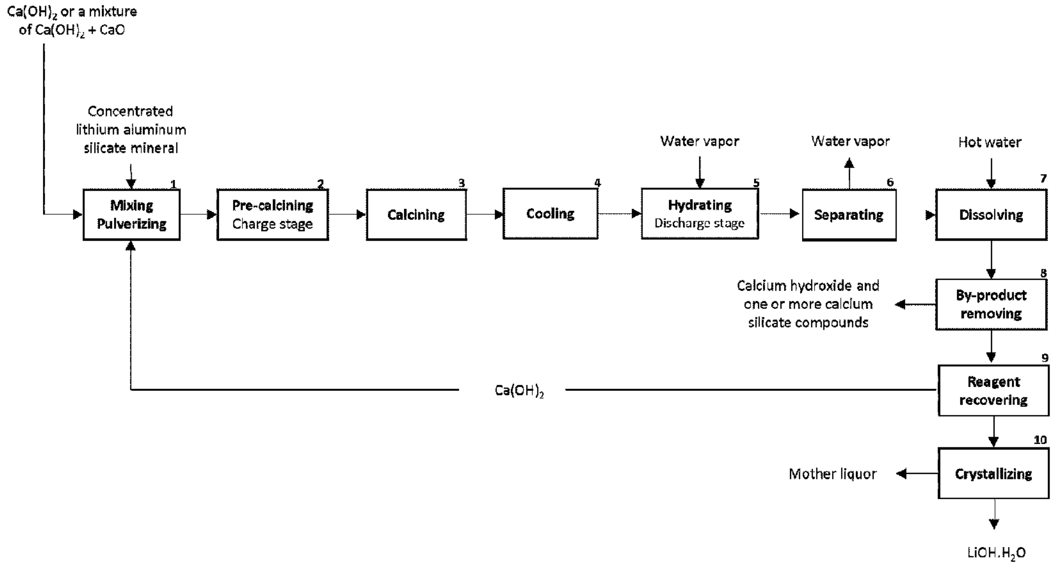
(54) Titre : METHODE POUR CONVERTIR DU LITHIUM EN FORME SOLUBLE A PARTIR DE MINERAIS DE SILICATE DE LITHIUM A L'AIDE D'UN SYSTEME DE CHAUFFAGE CHIMIQUE INTRINSEQUE

(54) Title: METHOD TO CONVERT LITHIUM IN SOLUBLE FORM FROM LITHIUM SILICATE MINERALS BY THE USE OF AN INTRINSIC CHEMICAL HEAT SYSTEM



(57) Abrégé/Abstract:

The present description relates to a method for producing lithium hydroxide and a by-product containing a mixture of calcium hydroxide and calcium silicate compounds from concentrated lithium aluminum silicate minerals. The method described herein consists generally in the mixture of mineral and calcium reagent followed by thermal treatments. The solid mass is cooled and hydrated by water vapor to convert free oxides into hydroxides. The solid-H_2O vapor mixture is separated and the solid recovered is leached with hot water to dissolving soluble salts. The residual solid is removed from the slurry and is the by-product. The salts solution is partly evaporated and calcium hydroxide is recovered. The solution is evaporated in part to obtained and recovered crystals of lithium hydroxide monohydrate.

ABSTRACT OF THE DISCLOSURE

The present description relates to a method for producing lithium hydroxide and a by-product containing a mixture of calcium hydroxide and calcium silicate compounds from concentrated lithium aluminum silicate minerals. The method described herein consists generally in the mixture of mineral and calcium reagent followed by thermal treatments. The solid mass is cooled and hydrated by water vapor to convert free oxides into hydroxides. The solid-H_2O vapor mixture is separated and the solid recovered is leached with hot water to dissolving soluble salts. The residual solid is removed from the slurry and is the by-product. The salts solution is partly evaporated and calcium hydroxide is recovered. The solution is evaporated in part to obtained and recovered crystals of lithium hydroxide monohydrate.

METHOD TO CONVERT LITHIUM IN SOLUBLE FORM FROM LITHIUM SILICATE MINERALS BY THE USE OF AN INTRINSIC CHEMICAL HEAT SYSTEM

TECHNICAL FIELD

[0001] The present disclosure relates to the recovery of lithium from concentrated lithium aluminum silicate minerals using pyrometallurgical and intrinsic chemical heat system techniques producing lithium hydroxide and a by-product containing calcium hydroxide and calcium silicate compounds under a desired form.

BACKGROUND

[0002] In most case, lithium-bearing minerals occurs in pegmatite mines and include spodumene, petalite and lepidolite, such lithium aluminum silicates. Their respective formula are $Li_2O.Al_2O_3.4SiO_2$, $Li_2O.Al_2O_3.8SiO_2$ and $LiF.KF.Al_2O_3.3SiO_2$. Nowadays, lithium as its major applications in batteries and cells, in the ceramic and glass industry and in lubricating greases trade. In the last decade, overall lithium consumption has increased significantly resulting in a grow demand. Lithium is used as a mineral concentrate or as a simple compounds, such carbonate or chloride. If in the past the concentrate was the main form of lithium sale, now the trend changes. Increasingly lithium compounds are being consumed. As the chief ore and with the growing interest in lithium, lithium aluminum silicate minerals is again taken into consideration for producing lithium products, more particularly lithium hydroxide.

[0003] There are two industrial processes of lithium recovery from lithium aluminum silicate minerals: acid pathway and basic pathway. Both involve high temperature reaction and yield salts readily interconvertible.

[0004] In the usual acid processes cited in the U.S. patent 2,020,854 and as described in the U.S patent 2,516,109 the ore is calcined at around 1050°C to convert the naturally occuring α-spodumene to β-spodumene. This change in molecular structure is accompanied by a severe decrepitation. The calcined material is roasted at 250°C with sulfuric acid in a stoichiometric portion of hydrogen-lithium at about 40 per cent in excess. Then, the lithium sulfate is leached out with hot water. By increasing pH, the impurities in solution are precipitated. Insoluble portion is remove by filtration. Lithium is recovered as a sulfate after neutralizing treatment with same acid. Otherwise, lithium is precipitated as a carbonate by reaction with soda ash or carbon dioxide bubbling.

[0005] This method has some disadvantages, which make it expensive. The acid roasting step results in a dissolution of other metals along with the lithium and in a significant proportion, such iron and aluminum. Although the ore is generally concentrated initially, a content of penalty iron oxide remains with the silicate mineral and is thus leached. Aluminum contained in the ore is also attacked by the acid. To neutralize the free acid in solution and precipitate unwanted elements, reagent consumption is significant. Also, the calcination temperature over 1000°C requires high energy consumption.

[0006] Lithium sulfate solution can be subject to electrochemical treatment using exchange membranes as presented by A. D. Ryabtsev and al. for additional purification. Lithium hydroxide solution, diluted sulfuric acid, oxygen and hydrogen are reaction products.

[0007] By the other pathway, lithium bearing minerals are calcined in the presence of a basic oxide between 800 and 1000°C. As describe in the U.S. patent 2,020,854, calcium carbonate or calcium oxide is mixed with the ore in a proportion around two to one. Then, the solid is leached with hot water to solubilise lithium and a part of calcium too. The later in the aqueous solution is precipitated by adding soluble carbonate or bubbling carbon dioxide gas therethrough. The solid-liquid mixture is separated by known methods. Hydrochloric acid is poured into the lithium solution in a sufficient amount to neutralise it and convert salts to chlorides. After concentration of the solution, a commercially usable lithium chloride is obtained.

[0008] By this method, calcium oxide used for calcination treatment is in a large amount. In addition, the calcium carbonate precipitate is not recovered, but remove with insoluble portion of the ore. Sadly, the authors did not specify the efficiency of lithium ore conversion by its reaction with calcium material. The operational parameters of each step are often incomplete or unspecified.

[0009] In the U.S. patent 2,662,809, the ore is firstly calcined between 1000 and 1300°C with an oxide from the group of alkali or alkaline-earth metal or salts forming these oxides during treatment at a temperature to partially or totally fuse the mass. In the mixture, the oxide material is present in a too small amount to bring about a sufficient solubility of the calcined product in water to readily leach lithium salts. Thus, the solid is mixed with a concentrate aqueous electrolyte solution, for example sodium chloride, under super atmospheric pressure to dissolve lithium. The slurry is filtrated to separate the insoluble residue. Sodium carbonate is added to lithium solution to precipitate impurities, such silico-aluminates. After removing them, lithium is recovered under carbonate form by addition of a further amount of reagent.

[0010] This way to recover lithium from minerals alters its crystallized nature and composition by chemical reactions at elevated temperature, such calcination and leaching steps. More, part of the silica is solubilized and becomes an additional impurity that must be removed from the aqueous solution.

[0011] Overall, the methods described are regardless of the economic potential of silicate secondary products. Also, warmth recovery and transfer from heat treatments are not maximized. The lithium is recovered under sulfate, chloride or carbonate form.

REFERENCES CITED

U.S. patent 2, 020, 854 Method of recovering lithium from its ores

U.S. patent 2, 516, 109 Method of extracting lithium values from spodumene ores

U.S. patent 2, 662, 809 Method of recovering lithium compounds from lithium minerals

A. D. Ryabtsev and al., Preparation of high-purity lithium hydroxide monohydrate from technical-grade lithium carbonate by membrane electrolysis, Applied electrochemistry and corrosion protection of metals, Vol. 77, 2004.

SUMMARY

[0012] This invention relates to a method for separate lithium from concentrated lithium aluminum silicate minerals by the use of a powerful reagent. Another object of this invention is to provide an efficient method to convert the separate lithium in a soluble water form. Another object of this invention is to provide a cost-effective method by the use of an intrinsic chemical heat system and minimize in many different manners the energy consumption. It is a further object of the invention to provide a method to produce lithium hydroxide and marketable by-product contained calcium silicate compounds under a desired form.

BRIEF DESCRIPTION OF DRAWING

[0013] Figure 1 illustrates a schematic representation of a method to produce lithium hydroxide and a by-product contained a mixture of calcium hydroxide and one or more calcium silicate compounds from concentrated lithium aluminum silicate minerals.

DETAILED DESCRIPTION

[0014] There is provided a method to produce lithium hydroxide and a by-product contained a mixture of calcium hydroxide and one or more calcium silicate compounds from concentrated lithium aluminum silicate minerals comprising the steps of mixing and pulverizing the concentrated mineral and the alkaline calcium reagent obtaining an ultimate mixture of the two; pre-calcining the mixture producing calcium oxide in the blend; calcining the mixture obtaining a calcined mass containing calcium oxide, lithium oxide and one or more calcium silicate compounds; cooling the calcined mass obtaining a cooled mass; hydrating the cooled mass with water vapor producing a solid-H_2O_{vapor} mixture; separating the solid-H_2O_{vapor} mixture obtaining a solid containing calcium hydroxide, lithium hydroxide and/or lithium hydroxide monohydrate, one or more calcium silicate compounds and water vapor; dissolving soluble salts from the solid with hot water obtaining a slurry comprising a solid fraction and a liquid fraction; separating from the slurry the solid fraction containing calcium hydroxide and one or more calcium silicate compounds obtaining a by-product; recovering calcium hydroxide from the liquid fraction by water evaporation, precipitation then separation; introducing the calcium hydroxide recovered at mixing-pulverizing step; crystallizing lithium salt from liquid fraction by partial water evaporation; separating the crystals from the mother liquor obtaining lithium hydroxide monohydrate and a mother liquor with impurities; recovering and using heat released from calcining, cooling and hydrating steps to reduce the energy demand of the process; recovering and using water vapor used in excess and obtained by evaporation to reduce energy demand of the process.

[0015] The present method is effective for treating various concentrated lithium aluminum silicate minerals such as for examples, and not limited to, spodumene, petalite and lepidolite or mixtures thereof which is used as starting material. Beneficiation of lithium aluminum silicate minerals are known in the art and aims to concentrate the lithium value.

[0016] At high temperature in the presence of calcium oxide (CaO), lithium oxide (Li_2O) from spodumene is replaced to form a calcium aluminum silicate molecule ($Ca_2Al_2SiO_7$) or liberated to obtain calcium silicates ($CaSiO_3$, Ca_2SiO_4), but not restricted too. According to the lithium aluminum silicate mineral used, other silica compounds may be obtained. The reactions are evidenced by the fact that lithium oxide may next be converted by water vapor in hydroxide form, then dissolved with hot water such as described below.

[0017] Calcium oxide's specific surface area improve the yield of solid-phase reactions. A correlation is found between structural properties of calcium hydroxide ($Ca(OH)_2$) and the product of its thermic treatment. When calcium hydroxide is decomposed at intermediate temperatures, such between 375 and 525°C, the calcium oxide shows a higher specific surface area. This enhancement is considered at the pre-calcination stage. To promote the reaction with a concentrated mineral, the use of calcium hydroxide or a mixture of calcium hydroxide and calcium oxide is recommended. Calcium hydroxide comes from the reagent recovery step and the new quantity introduced.

[0018] Particle size influences exchange capacity by accessible surface. In the present method, thermal substitutions and reformulation reactions are accomplished in a solid phase. Hence they require fine grinding ore and reagent to give large surface area and facilitate the further reactions. The concentrate mineral and calcium hydroxide are mixed and pulverized together to obtain an ultimate mixture of the two **1**. A particle size smaller than 400 μm is considered efficient, more precisely a grain size spread between 25 and 354 μm. If a blend of calcium oxide and calcium hydroxide is used as reagent, the same procedure is applied to reach an optimum mixture.

[0019] The effective CaO-concentrated mineral mass ratio to separate lithium is less than 3.0, more particularly between 0.5 and 2.0. The total calcium reagent is expressed on an oxide base. Calcium is added in excess to the lithium content. The ratio is also selected according to the composition of the desired by-product: the more calcium, the more aluminum remains attached to silica.

[0020] The mixture is then fed into a continuous or discontinuous heating apparatus, for examples a rotary kiln or a furnace, to be heated within 375 to 525°C **2**. According to the fixed temperature, the roasted time varies between 5 to 30 minutes for complete decomposition of calcium hydroxide. Hot gas emitted from the calcination treatment may be used for example to carry out the pre-calcination.

[0021] If a blend of calcium hydroxide and calcium oxide is mixed with concentrated mineral, same residence time is applied for a given temperature at pre-calcination step to promote structure development of calcium oxide.

[0022] The CaO-concentrated lithium aluminum silicate mineral is next subjected to a thermal treatment at a temperature between 800 to 1000°C for 15 to 120 minutes **3**. Any of the well know types of continuous or discontinuous heating apparatus is used, for examples direct fired rotary calciner or furnace. Temperature and time are fixed according to the liberation rate of lithium. The method promotes the avoidance of the fused mass at these temperatures improving a secondary product more easily recoverable.

[0023] The calcined mass contained mostly one or more calcium silicate compounds, lithium oxide and calcium oxide is cooled at a temperature between 80 and 200°C **4**. The hot feed is chilled in any well know granulate cooling device where thermal energy is restored. This energy may be used for example to drying by-product or additionally drying calcium hydroxide recovered at later stage. If a coarse portion is formed during heat treatment, the calcined mass may be ground with a rotating ball mill equipped with a cooling device. Heat released is also recovered and introduced into the process.

[0024] The present method includes an intrinsic chemical heat loop, such dehydration-hydration alternating reaction using $Ca(OH)_2$-CaO adding to Li_2O hydration at pre-calcination and hydrating steps. The dehydration of calcium hydroxide discussed previously is called *charge stage* since energy is consumed by the following endothermic reaction.

$Ca(OH)_{2\,s} \rightarrow CaO_s + H_2O_g$ (1)

[0025] Through the hydration process carried out with water vapor, also called *the discharge stage*, exothermic reactions take place (reactions 2 to 5) and heat is released **5**.

$CaO_s + H_2O_g \rightarrow Ca(OH)_{2\,s}$ (2)

$Li_2O_s + H_2O_g \rightarrow 2LiOH_s$ (3)

$2LiOH_s + H_2O_g \rightarrow LiOH.H_2O_s$ (4)

$Li_2O_s + 3H_2O_g \rightarrow 2LiOH.H_2O_s$ (5)

[0026] The energy balance is largely positive since the hydration enthalpy is higher when steam is used as a reactant instead of liquid water. Free Li_2O and CaO react slowly in hot water but react vigorously with steam. Also the amount of oxide to hydrate versus the amount of hydroxide to dehydrate is much higher.

[0027] The hydration process carried out at a temperature below 200°C avoids the conversion of the newly formed LiOH into oxide according to the reaction below.

Iron oxide come from concentrated mineral is however inactive, so avoided further impurities dissolution at the leaching stage.

$2LiOH_{s} \rightarrow Li_2O_{s} + H_2O_{g}$ (6)

[0028] Specifically, the steam water and the hot solid mixture are brought into contact in a fluid bed reactor at atmospheric pressure. Steam is fed in a sufficient amount to act as a fluidizing gas and as a reactant with the free Li_2O and CaO contained in the mass. Otherwise, air or nitrogen could be used as a gas carrier of steam. Fluid bed reactor has for inherent advantages a uniform temperature gradient and ability to operate in continuous state. A heat exchanger located inside the reactor extract thermal power and can exploit the high heat transfer coefficients typical in fluidized beds. The solid-H_2O_{vapor} mixture is then separated with the aid of a cyclone **6**. The reaction heat released may be used for example to drive the steam cycle. Other methods for hydrating solid can be used, for example a conveyor belt with a chamber where water vapor is sprayed.

[0029] The solid mixture is then leached with water at a temperature between 70 and 100°C into one or more successive stirred device. This solid-liquid extraction is designed to dissolving soluble salts, essentially of lithium, potassium and sodium **7**. A part of calcium pass jointly into solution and is recovered at a later stage. The slurry is separated by know techniques **8**. Countercurrent extraction method could be an alternative way in which small amounts of water in continuous mode are sprayed to the mass. The residual solid consists mainly in a mixture of one or more calcium silicate compounds and calcium hydroxide. Traces of iron oxide and/or unreacted mineral could be present.

[0030] The alkaline solution is evaporated partly to precipitate dissolved calcium hydroxide as a recovered reagent step **9**. The removal of calcium is done by filtration or other know separation techniques. The hydroxide is dried and reintroduced at the mixing-pulverizing step. The amount to be recovered depends on the ratio used initially and the solubility of calcium hydroxide in water. The benefit of recovery is found in the production of reagent with better reaction characteristics obtained under pre-calcination conditions.

[0031] According to the CaO-concentrated mineral mass ratio, lithium aluminum compounds may be formed during calcination and then leachable by water. In this case, an additional impurity is found in solution.

[0032] In the aqueous solution at a pH above 4, Al^{3+} ions are hydrolyzed and the solubility of aluminum compounds formed are influenced by Li^+ in the system. In presence of high lithium ions content, a significantly lower solubility is observed and promote the removal of aluminum hydroxide species from the lithium rich solution by precipitation. At a molar ratio Li^+/Al^{3+} above 0.4, the lithium effect is noticed. The salts concentration is adjusted by evaporation while maintaining soluble lithium. Any of know separation equipment can be used to remove aluminium and calcium precipitated.

[0033] Lithium hydroxide monohydrate ($LiOH.H_2O$) is obtained from rich lithium solution by partial evaporation of water at atmospheric pressure or under vacuum **10**. The solubility of lithium hydroxide in water is much lower than that of the potassium and sodium hydroxides, which makes it possible to separate them. The crystals are removed from the mother liquor by a mechanical separation technique, for example dewatering system. Monohydrate product can be dehydrating to obtain lithium hydroxide.

[0034] Water vapor from solid-H_2O_{vapor} separation, reagent recovering and crystallizing steps is recovered and reintroduced into the process to minimize water consumption and energy to produce it.

[0035] The method described herein allows de production of lithium hydroxide and a marketable by-product which exhibits economic benefits mainly associated with low energy costs. By coupling heat emission and heat recovery, the energy demand of the process is reduced and profitability is improved. Heat sources come from calcination of CaO-concentrated mineral, calcined mass cooling and cooled mass hydrating.

[0036] As a source of calcium and silicate, the by-product could be used as a flux in pyrometallurgical recovering process of platinum-group metals (PGM) from spent automotive catalysts. The classic ceramic catalysts are initially mixed with fluxes, collector and reductant during smelting and a PGM-collector alloy is obtained which further undergoes purification.

[0037] For another example of industrial application, the by-product has a potential value as an ingredient of cement to replace basic raw materials used in its production. In brief, cement is made by heating a carefully dosed mixture of limestone (any rock composed mostly of calcium carbonate), clay (natural rock based on silicates and/or aluminosilicates) and sometimes sand in a rotary kiln to a temperature around 1450ºC. The result is an intermediate product called clinker. Calcination of limestone emits carbon dioxide, a greenhouse gases. Also, quarries exploitation requires sound management with respect to the preservation of the environment. The use of value products helps to preserve the reserves.

[0038] The present invention will be more readily understood by referring to the following examples which are given to illustrate the invention rather than to limit its scope.

EXAMPLE 1

[0039] To demonstrate the increase of specific surface area of the calcium oxide, a hydration-dehydration test was carried out and this characteristic was measured by the BET method. A powder reagent was spread on a plate and hydrated by a jet of water vapor. The product was leached with water at 80°C then dried to constant weight at 120°C. The calcium hydroxide was dehydrated at 400°C for 20 minutes. This treatment represents the hydrating, leaching and pre-calcining steps that would occur to calcium oxide by this method. The specific surface are of calcium oxide has increased from 1.86 m^2/g initially to 18.02 m^2/g, such about 10 times.

EXAMPLE 2

[0040] Pre-calcination and calcination of a mixture of calcium hydroxide and concentrated spodumene in a muffle furnace was completed to view the reaction products. The sample was analysed by x-ray powder diffraction (XRPD). The mineral contained 5.76% Li_2O.

[0041] Calcium oxide was first hydrated under a jet of water to convert it into hydroxide. The reagent was well mixed with the mineral. The CaO-concentrated spodumene mass ratio was 1.0. The temperature was first fixed at 400°C for 20 minutes and next increased to 975°C for an additional 90 minutes. The mass lost was 15.4%.

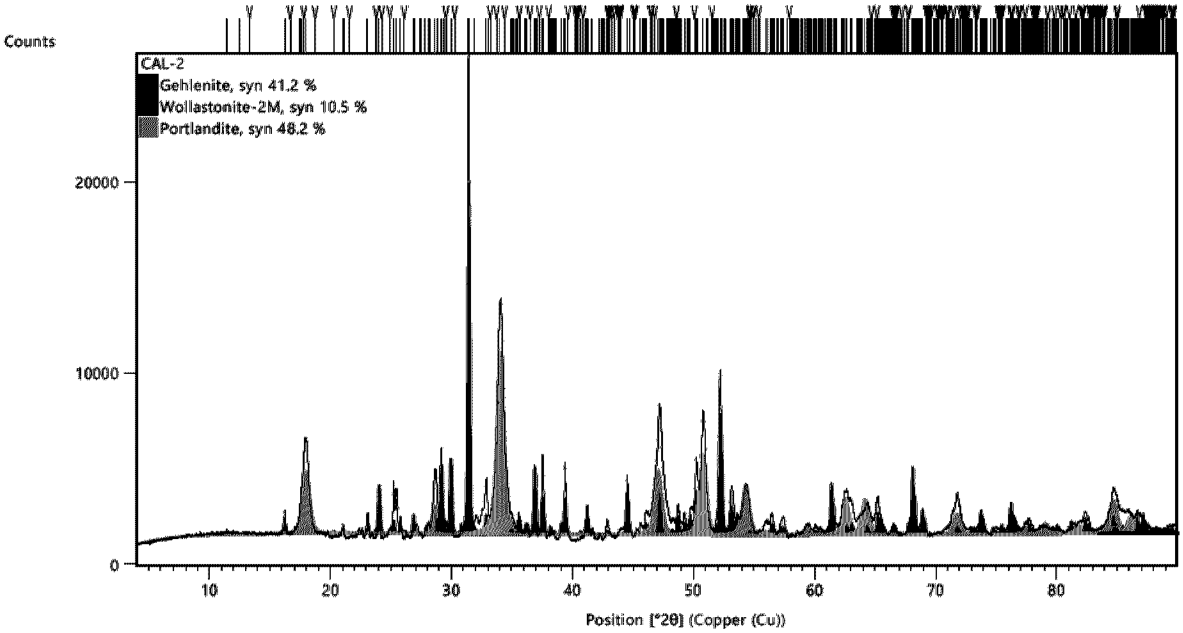
[0042] The sample was lightly crushed and analyzed under the conditions presented in the table 1. A search in a database indicates three crystalline phases as the main constituents: a calcium aluminum silicate (gehlénite: $Ca_2Al_2SiO_7$), a calcium silicate (wollastonite-2M: $CaSiO_3$) and the portlandite ($Ca(OH)_2$) also called calcium hydroxide. The graph 1 beneath shows a semi-quantification on these three phases by the Rietveld method. The result indicate that portlandite and gehlenite are the majority constituents of the sample. Spodumene was not observed which suggests that it fully reacted with the reagent.

[0043] The presence of calcium hydroxide versus calcium oxide may be explained by air exposure and moisture content prior to analysis.

Table 1

XRPD analysis experimental conditions

Instrument :	Malvern PanAlytical Empyrean 3	
Géométrie :	Bragg Brentano θ - θ	
Radiation :	CuKα, λ = 1.54178 Å	
Détecteur :	PIXcel^{3D} (255 canaux)	
Paramètres d'acquisition :	2θ initial	4°
	2θ final	90°
	Pas angulaire	0.013°
	Temps d'acquisition par pas angulaire	0.8 s (198 s pour 255 canaux.)
	Temps total d'acquisition	1 heure 30


Counts
CAL-2
Gehlenite, syn 41.2 %
Wollastonite-2M, syn 10.5 %
Portlandite, syn 48.2 %
20000
10000
0
10
20
30
40
50
60
70
80
Position [°2θ] (Copper (Cu))

Graph. 1

WHAT IS CLAIMED IS

1. A method to produce lithium hydroxide and a by-product contained calcium hydroxide and one or more calcium silicate compounds from concentrated lithium aluminum silicate minerals, comprising the steps of:

   a) mixing and pulverizing the concentrated mineral and an alkaline calcium reagent to a grain size smaller than 400 μm obtaining an ultimate mixture of the two;

   b) pre-calcining at a temperature between 375 and 525°C the mixture producing calcium oxide in the blend;

   c) calcining the mixture at a temperature within a range of 800 and 1000°C obtaining a calcined mass containing calcium oxide, lithium oxide and one or more calcium silicate compounds;

   d) cooling the calcined mass at a temperature between 80 and 200°C obtaining a cooled mass;

   e) hydrating the cooled mass with water vapor producing a solid-H_2O_{vapor} mixture;

   f) separating the solid-H_2O_{vapor} mixture obtaining a solid containing calcium hydroxide, lithium hydroxide and/or lithium hydroxide monohydrate, one or more calcium silicate compounds and water vapor;

   g) dissolving soluble salts from the solid with water at a temperature between 70 and 100°C obtaining a slurry comprising a solid fraction and a liquid fraction;

   h) removing by separation from the slurry the solid fraction containing calcium hydroxide and one or more calcium silicate compounds obtaining a by-product;

   i) recovering calcium hydroxide from the liquid fraction by partial water evaporation, precipitation then separation;

   j) introducing the calcium hydroxide recovered at mixing-pulverizing step;

k) crystallizing lithium salt from liquid fraction by partial water evaporation;

l) separating the crystals from the mother liquor obtaining lithium hydroxide monohydrate and mother liquor with impurities;

m) recovering and using heat released from calcining, cooling and hydrating steps to reduce the energy demand of the process;

n) recovering and using water vapor used in excess and obtained by evaporation to reduce energy demand of the process.

2. The method of claim 1, wherein the concentrated lithium aluminum silicate mineral is concentrated spodumene, petalite, lepidolite or mixtures thereof.

3. The method of claim 1, wherein the alkaline calcium reagent is calcium hydroxide or a mixture of calcium hydroxide and calcium oxide.

4. The method of any one of claims 1-3, wherein the concentrated mineral and the alkaline calcium reagent are mixed and pulverized to obtain a grain size spread between 25 and 354 μm.

5. The method of any one of claims 1-4, wherein CaO-concentrated mineral mass ratio is less than 3.0 under which total alkaline calcium reagent is expressed on an oxide base.

6. The method of claim 5, wherein CaO-concentrated mineral mass ratio is between 0.5 and 2.0 under which total alkaline calcium reagent is expressed on an oxide base.

7. The method of any one of claims 1-6, wherein the mixture of alkaline calcium reagent and concentrated mineral is pre-calcined for 5 to 30 minutes promoting specific surface area development of calcium oxide.

8. The method of any one of claims 1-7, wherein the mixture of CaO-concentrated mineral is calcined for 15 to 120 minutes.

9. The method of any one of claims 1-8, wherein the cooled mass is hydrated in a fluid bed reactor at atmospheric pressure equipped with a heat exchanger.

10. The method of claim 9, wherein water vapor is used in a sufficient amount to act as a fluidizing gas and as a reactant.

11. The method of claim 10, wherein air or nitrogen is used as a gas carrier of water vapor.

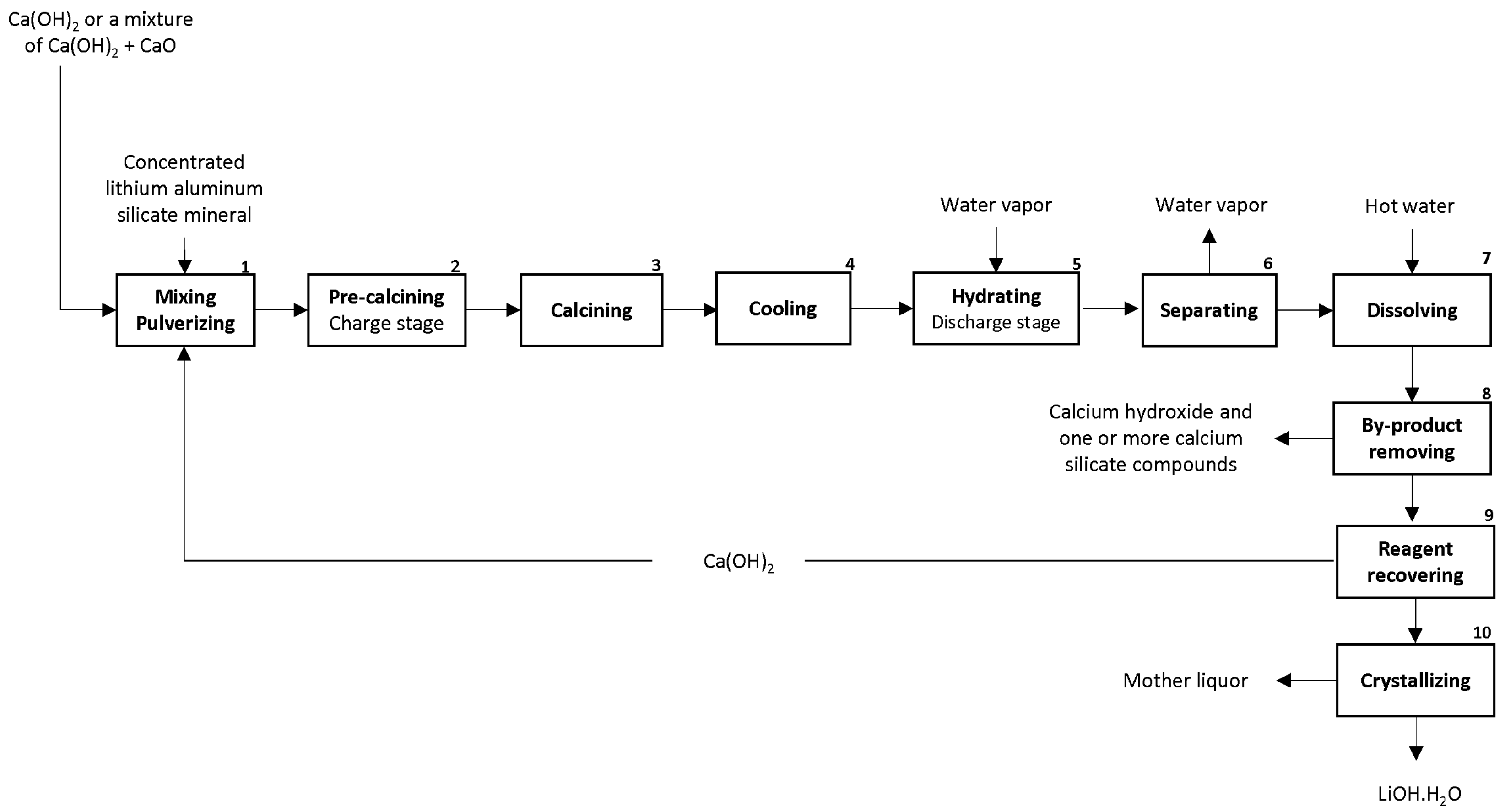
12. The method of any one of claims 1-8, wherein the cooled mass is hydrated in a conveyor belt with a chamber where water vapor is sprayed.

13. The method of claim 1, wherein an intrinsic chemical heat loop is included from dehydration-hydration alternating reactions using $Ca(OH)_2$-CaO adding to Li_2O hydration at pre-calcination and hydration steps.

14. The method of any one of claims 1-13, wherein aluminum hydroxide's species and calcium hydroxide are removed from the liquid fraction by partial water evaporation, precipitation then separation.

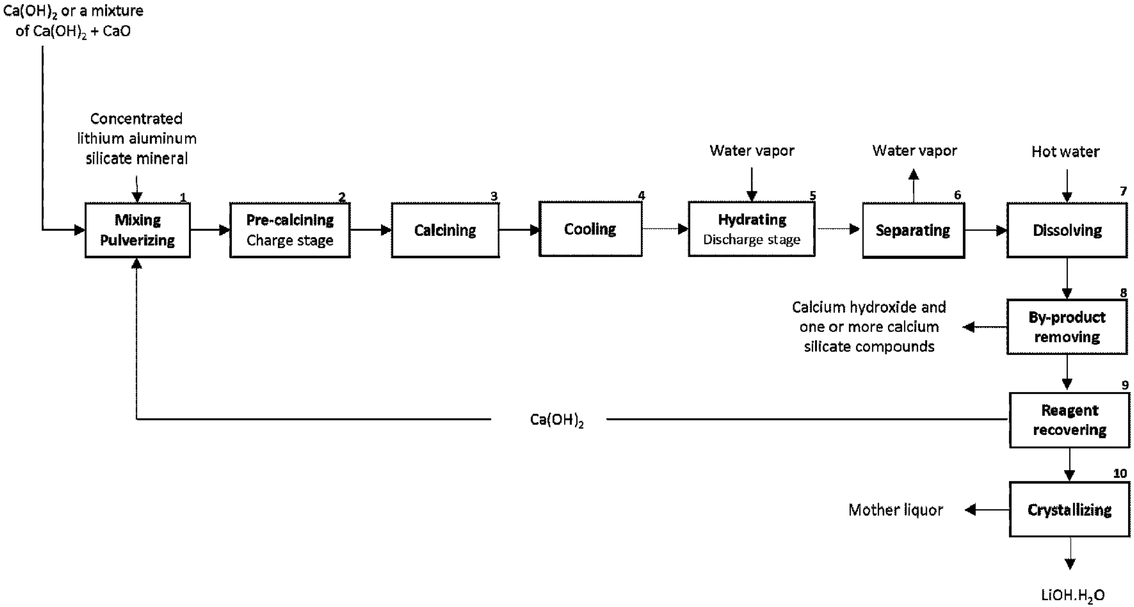
15. The method of claim 14, wherein molar ratio of Li^+/Al^{3+} in solution is above 0.4.

16. The method of any one of claims 1-15, wherein the by-product is used as a flux in pyrometallurgical recovering process of platinum-group metals (PGM) from spent automotive catalysts.



$Ca(OH)_2$ or a mixture of $Ca(OH)_2$ + CaO
Concentrated lithium aluminum silicate mineral
Water vapor
Water vapor
Hot water
1
Mixing Pulverizing
2
Pre-calcining Charge stage
3
Calcining
4
Cooling
5
Hydrating Discharge stage
6
Separating
7
Dissolving
8
By-product removing
Calcium hydroxide and one or more calcium silicate compounds
9
Reagent recovering
$Ca(OH)_2$
10
Crystallizing
Mother liquor
$LiOH.H_2O$

Fig. 1


$Ca(OH)_2$ or a mixture of $Ca(OH)_2$ + CaO
Concentrated lithium aluminum silicate mineral
1
Mixing Pulverizing
2
Pre-calcining Charge stage
3
Calcining
4
Cooling
Water vapor
5
Hydrating Discharge stage
Water vapor
6
Separating
Hot water
7
Dissolving
8
By-product removing
Calcium hydroxide and one or more calcium silicate compounds
9
Reagent recovering
$Ca(OH)_2$
10
Crystallizing
Mother liquor
$LiOH.H_2O$