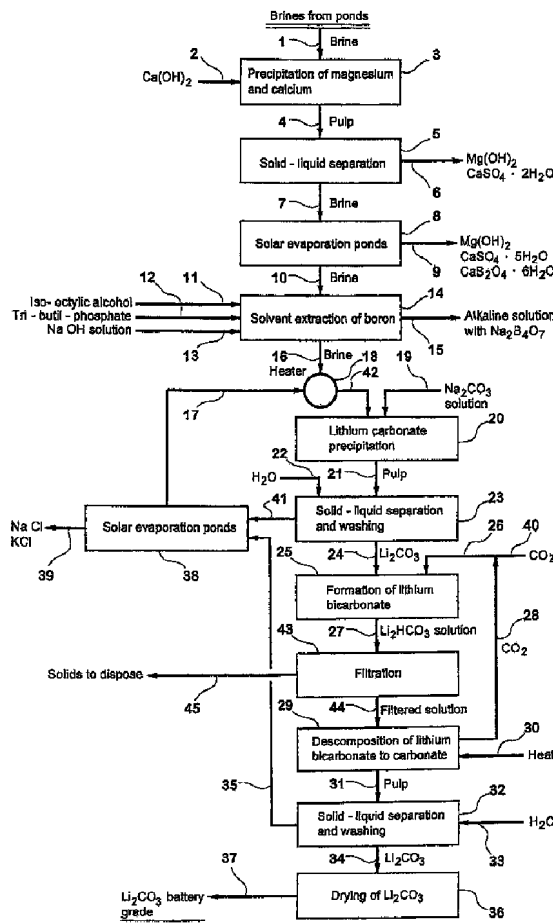




(22) Date de dépôt/Filing Date: 2011/12/20
(41) Mise à la disp. pub./Open to Public Insp.: 2013/04/24
(30) Priorité/Priority: 2011/10/24 (AR20110103922)

(51) Cl.Int./Int.Cl. *C01D 15/08* (2006.01)
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(54) Titre : PRODUCTION DE CARBONATE DE LITHIUM A PARTIR D'EAU SALEE
(54) Title: LITHIUM CARBONATE PRODUCTION FROM BRINE



(57) **Abrégé/Abstract:**

High purity battery-grade lithium carbonate can be produced from natural or industrial brines by (i) precipitating the magnesium with calcium hydroxide, (ii) removing the boron by solvent extraction, (iii) precipitating lithium carbonate with sodium carbonate; (iv)



(57) **Abrégé(suite)/Abstract(continued):**

transforming the lithium carbonate into lithium bicarbonate with carbonic acid, (v) decomposing the lithium bicarbonate into high purity lithium carbonate by heating the solution. The re-precipitation of lithium carbonate through the formation of lithium bicarbonate allows removal of most of the residual impurities from the lithium carbonate and production of a high purity battery-grade lithium carbonate.

ABSTRACT

High purity battery-grade lithium carbonate can be produced from natural or industrial brines by (i) precipitating the magnesium with calcium hydroxide, (ii) removing
5 the boron by solvent extraction, (iii) precipitating lithium carbonate with sodium carbonate; (iv) transforming the lithium carbonate into lithium bicarbonate with carbonic acid, (v) decomposing the lithium bicarbonate into high purity lithium carbonate by heating the solution. The re-precipitation of lithium carbonate through the formation of lithium bicarbonate allows removal of most of the residual impurities from the lithium
10 carbonate and production of a high purity battery-grade lithium carbonate.

LITHIUM CARBONATE PRODUCTION FROM BRINE

BACKGROUND OF THE INVENTION

(i) Field of the Invention

5 [0001] The present invention relates to a process for producing high purity, battery-grade lithium carbonate from natural or industrial brines.

(ii) Description of the Related Art

[0002] Lithium, the 3rd element of the Periodic Table, the lightest of all metals and the 32nd in abundance in the earth crust, is becoming a metal that can play an important
10 role in the rapidly developing area of batteries for electric vehicles.

[0003] In the past, lithium has steadily increased its applications, mainly for pharmaceutical uses at the beginning of the 20th Century, up to the present time with broad uses in ceramics, glasses, aluminium industry, rubber, chemicals and alloys and in the rapidly developing field of lithium batteries. The use in lithium batteries is expected to
15 overcome all the other lithium applications by the middle of the 21st Century.

[0004] Lithium can be extracted from several sources. One, which is an important source of lithium, is brine from salt lakes, geysers and salt mines. These brines vary broadly in composition and lithium content, the chloride-based and sulfate-based brines being the most abundant. Table 1 shows the typical chemical composition of brines from
20 several sources around the world.

Table 1: Chemical composition of natural brines, salt lakes and the ocean (wt-%).

Source	Li	Mg	Ca	Na	K	Cl	B
Silver Peak, USA	0.02	0.02	0.71	6.3		10.1	0.005
Dead Sea, Israel	0.002	4.0	0.06	3.1	0.6	16.1	0.003
Ocean (average)	0.0001	0.12	0.04	1.05	0.04	1.92	0.0004
Sakar de Atacama, Chile	0.15- 0.20	1-1.4	0.04- 1.5	5.7-7.2	1.7-1.9	16- 17	0.04- 0.05
Salar de Cauchari, Argentina	0.05	0.13	0.03	9.8	0.47	15.5	0.47

5 [0005] The mineral spodumene ($\text{LiAl}(\text{SiO}_3)_2$) is another important source of lithium containing 3.73 wt-% lithium. Spodumene is a pyroxene (double silicate of lithium and aluminium) which has been a source for several lithium compounds, being the main mineral of lithium exploited at the present time. Other lithium minerals exploited commercially are petalite ($\text{LiAlSi}_4\text{O}_{10}$) with 2.27 wt-% Li and lepidolite of variable
10 composition. These two minerals are used as additives to glass and ceramics but are not a source of lithium compounds or metal at the present time.

[0006] There are many other lithium minerals. Since lithium is extremely reactive (it has only one electron in its outer shell), it can form compounds with almost all the elements of the Periodic Table. Lithium chloride, bromide and iodide are very soluble in
15 water. This effect is reflected in the lithium content of sea water (10^{-4} wt-%) which could be potentially the largest source of lithium available on earth.

[0007] The treatment of brines from salars and lakes varies broadly according to their composition. In general, chloride-based brines contain significant amounts of magnesium which must be removed before precipitating the lithium. Other impurities
20 which also must be removed are boron, calcium and sodium depending upon the final application of the lithium compound. Battery-grade metallic lithium requires less than 6×10^{-4} wt-% of sodium, since this metal can oxidize violently in presence of oxygen, producing a fire hazard. Magnesium also must be present in less than 5×10^{-3} wt-% since

it accumulates in the electrolyte in the molten salts electrolytic production of metallic lithium, short-circuiting the cells. Production of lithium metal is accomplished by using a molten electrolyte of 55 wt-% KCl and 45 wt-% LiCl at 800-850°C under an argon atmosphere.

5 [0008] As noted before, each brine may need particular treatment, therefore several processes have been developed. Most of the patented processes for chloride based brines follow a route that involves the removal of boron by solvent extraction; dilution of the brine with mother liquor; precipitation of the magnesium in two steps and final precipitation of the lithium as carbonate.

10 [0009] For chloride-based brines such as those from the Salar de Atacama in northern Chile, U.S. Pat. No. 5,993,759 describes a process for concentrating brines containing from 5 to 7 wt-% lithium, 0.5 wt-% boron and 1 to 2.5 wt-% magnesium, the latter being two the main contaminants. The process includes an initial step for boron removal by solvent-extraction using a blend of aliphatic alcohols in an aromatic solvent.
15 The boron-depleted brine is then diluted with mother liquor to obtain 0.8 - 0.9 wt-% lithium. This is done to avoid excessive precipitation of lithium, since the next step in the process is the precipitation of most of the magnesium as carbonate (MgCO_3) with soda ash (Na_2CO_3).

[0010] After solid - liquid separation, a second step of magnesium precipitation is
20 performed by using lime milk ($\text{Ca}(\text{OH})_2$) to precipitate the remaining magnesium as magnesium hydroxide. The purified brine is then treated with soda ash at 80-90°C to precipitate lithium carbonate (Li_2CO_3), which shows inverse solubility with temperature. The lithium carbonate is further hot filtered, washed and dried.

[0011] This basic process has also been proposed, with some differences, for others
25 brines. For example, U.S. Pat. No. 5,219,550 and U.S. Pat. No. 6,921,522 describe processes similar to the basic process with additional steps to reduce specific impurities such as calcium and sodium.

[0012] Battery-grade lithium metal requires a high purity lithium chloride which can be produced from lithium carbonate or lithium hydroxide. Electrolytic grade lithium chloride requires less than 0.0006 wt-% sodium and less than 0.005 wt-% magnesium, which represents a lithium carbonate of 99.4 wt-% purity or greater if lithium chloride is obtained from lithium carbonate.

[0013] Lithium carbonate produced using conventional processes like those described in U.S. Pat. No. 5,993,759; U.S. Pat. No. 5,219,550; U.S. Pat. No. 4,261,960; U.S. Pat. No. 4,036,718 and U.S. Pat. No. 4,243,392 normally contain 99.2 wt-% of Li_2CO_3 , with 0.2 -0.3 wt-% sodium and 0.05 - 0.1 wt-% magnesium, which makes it unsuitable for producing battery-grade lithium due to presence of these deleterious metals.

[0014] There are several patents to purify both lithium chloride and lithium carbonate. For instance, U.S. Pat. No. 4,980,136 describes a process to produce battery-grade lithium chloride from a concentrated brine using solvent extraction with an aliphatic alcohol, which is evaporated leaving high grade lithium chloride crystals.

[0015] Other methods such as the one disclosed in U.S. Pat. No. 4,859,343 use ion exchange resins to remove sodium ions from chloride brines.

Since it is very difficult to produce lithium chloride with less than 0.16 wt-% sodium directly from lithium carbonate, the carbonate is generally transformed into lithium hydroxide and then into lithium chloride, or the lithium carbonate is reacted with hydrochloric acid to produce lithium chloride, which can be further purified by successive crystallization. This processes, although highly intensive in steps, produces lithium chloride suitable for electrolysis, with less than 0.0006 wt-% sodium.

Summary of the Invention

[0016] The removal of magnesium with lime before the removal of boron provides the advantage of avoiding lithium co-precipitation due to the use of soda ash to remove magnesium as carbonate. This alternative can be applied when the brine contains 0.9-1.2

wt-% lithium, since in addition to the virtually complete precipitation of magnesium as magnesium hydroxide, it also precipitate significant amounts of calcium as gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and boron as calcium borate ($\text{CaB}_2\text{O}_4 \cdot 6\text{H}_2\text{O}$), reducing the amount of boron required to be further removed by solvent extraction.

5 [0017] In that magnesium precipitation with lime leaves levels of magnesium close to zero in the brine, additional steps are not necessary to remove residual magnesium or to dilute the brine with mother liquor. Lithium carbonate can be precipitated directly from the magnesium and boron-free brine. Lithium carbonate can be further purified to reduce other impurities such as calcium and sodium by transforming lithium carbonate into
10 lithium bicarbonate (LiHCO_3) with carbonic acid (H_2CO_3) produced with carbon dioxide (CO_2). Upon further heating, the solution with lithium bicarbonate allows re-precipitating of a high-purity lithium carbonate, leaving the impurities in solution.

[0018] In order to produce battery-grade lithium carbonate, an integral process is disclosed in which the lithium carbonate is purified through the formation and
15 decomposition of lithium bicarbonate. The process starts with the precipitation of the magnesium from the brine with lime milk ($\text{Ca}(\text{OH})_2$) followed by further evaporation of the brine where additional magnesium, calcium and boron compounds are precipitated. The magnesium-depleted brine is then subjected to solvent extraction to remove the remaining boron. The purified brine is then reacted with a soda ash solution (Na_2CO_3) to
20 precipitate lithium carbonate at 80-100°C.

[0019] After filtering and washing the lithium carbonate cake, it is redissolved in cold CO_2 -saturated water solution containing carbonic acid to form soluble lithium bicarbonate.

[0020] The solution is filtered and then heated to decompose the bicarbonate back
25 to lithium carbonate, leaving the soluble impurities in solution and generating CO_2 which can be recirculated to the process. The lithium carbonate pulp is then filtered and the cake

washed and dried. The filtrate is returned to the solar evaporation ponds for further recovery of lithium values.

Brief Description of the Drawings

[0021] The process of the invention will now be described with reference to the
5 accompanying drawings, in which:

Figure 1 is a process flow diagram showing the production of battery-grade lithium carbonate in accordance with the present invention; and

Figure 2 shows the details of the process and equipment required to purify lithium carbonate to produce battery-grade lithium carbonate in
10 accordance with the present invention.

Detailed Description of the Process of the Invention

[0022] For a better understanding of the process, a detailed description thereof will be made on the basis of a preferred embodiment, which shall have only an illustrative and non-limiting character.

15 [0023] In order to produce battery-grade lithium carbonate, an exemplary process is disclosed in which the lithium carbonate is purified through the formation and decomposition of lithium bicarbonate with the brines typified in Tables 2 and 3.

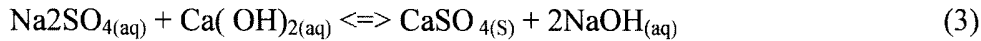
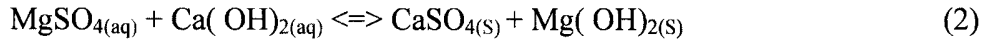
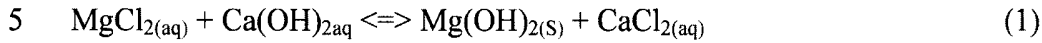
Table 2. Typical chemical composition of brines from Salar de Cauchari.

Element	Li	Cl	Na	K	Ca	Mg	SO₄⁼	H₃BO₃	H₂O
wt-%	0.05	14.70	9.80	4.81	0.00	0.14	0.197	0.60	72.33

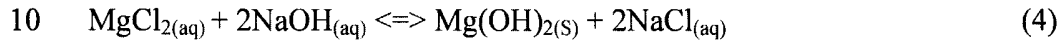
20 **Table 3. Typical chemical composition of concentrated brines from Salar de Cauchari.**

Element	Li	Cl	Na	K	Ca	Mg	SO₄⁼	H₃BO₃	H₂O
wt-%	0.39	12.7	5.41	2.70	2.52	9.91	5.92	2.53	55.42

[0024] In Figure 1, a concentrated brine 1 like the one shown in Table 3 is mixed and reacted with a saturated solution of lime milk ($\text{Ca}(\text{OH})_2$) 2 in a conventional reactor 3 such as an agitated vessel in a proportion sufficient to precipitate all of the magnesium chloride and sulfates, according to the following main reactions:



[0025] The NaOH formed by reaction (3) reacts with MgCl_2 to form $\text{Mg}(\text{OH})_2$ according to the reaction:



[0026] All these reactions are spontaneous since their' standard free energy of reaction, in a broad range of temperature, is negative. For instant, at 20°C, $\Delta G^\circ_1 = -21.4$ kcal; $\Delta G^\circ_2 = -27.0$ kcal; $\Delta G^\circ_3 = -27.1$ kcal and $\Delta G^\circ_4 = -43.2$ kcal, respectively. In this form, magnesium is virtually completely removed from the brine since the value of the solubility product K_{sp} of magnesium hydroxide formed at only 5.61×10^{-12} is very small.

[0027] The pulp 4 produced is then subjected to conventional solid-liquid separation 5, such as settling and filtering, to obtain magnesium free brine 7, and precipitated $\text{Mg}(\text{OH})_2$ and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ solids 6. The filtered brine 7 is further concentrated by solar evaporation in ponds 8 where additional salts 9 are precipitated, such as brucite ($\text{Mg}(\text{OH})_2$), gypsum ($\text{CaSO}_4 \cdot 5\text{H}_2\text{O}$), calcium borate ($\text{CaB}_2\text{O}_4 \cdot 6\text{H}_2\text{O}$) and halite (NaCl).

[0028] The concentrated brine 10, with a lithium content of 0.8 - 1.2 wt%, is then subjected to a conventional solvent extraction step 14 to remove the remaining boron. Table 4 shows the typical composition of concentrated brine from Salar de Cauchari obtained by solar evaporation entering the solvent extraction step.

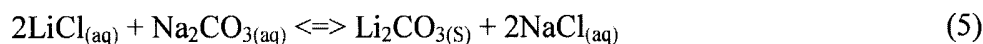
Table 4. Typical chemical composition of concentrated brine from Salar de Cauchari entering the solvent extraction process.

Element	Li	Cl	Na	K	Ca	Mg	SO ₄ ⁼	B	H ₂ O
wt-%	0.72	14.2	6.86	4.20	0.016	0.008	2.97	0.70	70

[0029] In this step, the brine pH is reduced from 11 to 7 with hydrochloric acid and then the brine is subjected to a conventional solvent extraction process 14 to remove the boron in one or more extraction stages using an aliphatic alcohol such as iso-octylic alcohol 11 with a 5 to 20 vol-% of a phase modifier such as tributyl-phosphate 12 dissolved in an aromatic solvent such as Escaid™ 110 in a ratio extractant:solvent from 1:10 to 10:1 for a total contact time of 1 to 60 minutes, a total setting time of 1 to 120 minutes and at a temperature from 0 to 50°C, using an organic:brine ratio of 6:1 to 1:5 at a pH of from 1 to 7, measured for a dilution of the brine in water of 1:10. The charged organic extractant is then subjected to a conventional re-extraction step in one or more re-extraction stages using an alkaline solution 13 of sodium hydroxide with a concentration of 0.01 to 3 mol/L using an organic:aqueous ratio of 1:5 to 5:1 for a total contact time of 1 to 60 minutes and a total setting time of 1 to 120 minutes at a temperature of 0 to 50°C. The alkaline solution 15 exiting the solvent extraction process 14 contains the boron as sodium borate (Na₂B₄O₇), and can be sent to evaporation ponds.

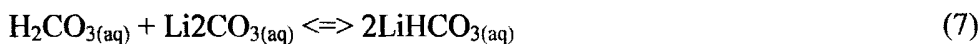
[0030] The boron-free brine 16 with less than 0.001 wt-% boron is further heated to 70-100°C in a conventional heat exchanger 18, and the hot brine 42 is sent to a lithium carbonate precipitation step 20 where it is reacted with an aqueous solution of 20 to 30 wt-% of soda ash (sodium carbonate, Na₂CO₃) 19 at a pH of 8 to 12. Reaction takes place in one or more conventional agitated and thermally insulated vessels for a reaction time of 5 to 150 minutes at a temperature of 70-100°C, since lithium carbonate shows an inverse solubility with temperature, being 7.2 g/L at 100°C and 15.4 g/L at 0°C.

[0031] The reaction that occurs in step 20 is the following:



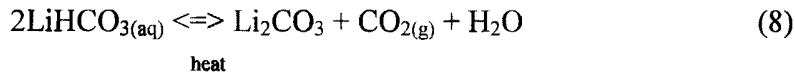
[0032] The hot pulp 21 at 70-100°C is further subjected to a conventional solid – liquid separation step 23 such as settling and filtering, maintaining the temperature of the pulp and the cake at 50-95°C. The cake of lithium carbonate (Li₂CO₃) is washed with 50-95°C demineralized water 22. The filtrate and wash water filtrate 41 is sent to solar evaporation ponds 38 to precipitate additional salts 39 such as halite (NaCl). The concentrated brine 17 from the solar ponds is returned to the heat exchanger 18 together with the concentrated brine 16 to recover additional lithium.

[0033] The lithium carbonate cake 24 is then dissolved in cold water at 0-30°C. As it was mentioned before, at 0°C the solubility of the lithium carbonate is 15.4 g/L. The transformation of lithium carbonate into bicarbonate and the decomposition steps and equipment involved are described later in detail. The dissolution is performed in a conventional agitated reactor 25 for a reaction time of 1 to 120 minutes in which a conventional gas diffuser inside the reactor allows injection of gaseous carbon dioxide (CO₂) 26 at a pressure of 1 to 5 atmospheres, which reacts with water to form carbonic acid (H₂CO₃) which in turn reacts with the dissolved lithium carbonate to form lithium bicarbonate, according to the following reactions:



[0034] Lithium bicarbonate has a much larger solubility than lithium carbonate, with 58 g/L at 0°C or 52 g/L at 10°C.

[0035] The solution 27 containing the dissolved lithium bicarbonate is then filtered in a conventional filter i.e. a press filter 43. The filtered solution 44 is then fed into a reaction vessel 29 where heat 30 is added by means of steam heating coils or other conventional method to heat the solution to a temperature of 50 to 100°C, a temperature at which lithium bicarbonate decomposes to lithium carbonate with generation of gaseous carbon dioxide 28 which can be recirculated back to the process. The reaction that takes place is the following:



[0036] Above 50°C, carbonic acid has a very low solubility, with only 0.01 g/L at 95°C. All the main soluble impurities accompanying the lithium carbonate 24, mainly sodium chloride (NaCl), calcium chloride (CaCl₂) and residual sulfates remain in solution.

[0037] The pulp 31 generated, containing the precipitated purified lithium carbonate, is further subjected to a conventional liquid - solid separation step 32 such as thickening and filtering, maintaining the pulp and cake at a temperature of 50 to 95°C. The purified lithium carbonate cake is washed with two volumes of demineralized water 33 with a temperature of 50-95°C. The filtrate and wash water filtrate 35 is send to solar evaporation ponds 38 to precipitate impurities 39 and concentrate the brine, and to recover additional lithium 17 from the brine which is recirculated to the process. The final purified lithium carbonate cake 34 is then dried at 150-200°C in conventional equipment such as an indirect heated kiln 36 to obtain dry battery-grade lithium carbonate 37.

[0038] Figure 2 represents schematically the lithium carbonate purification step showing the operation and main equipment involved. Prior to the addition of the lithium carbonate cake into the reactor 102, demineralized water 100 at 0-30°C is added to the reactor 102. Lithium carbonate cake 105 is then fed into the reactor 102 which is a conventional closed agitated reactor with a conventional agitator 103 in which gaseous carbon dioxide 106 at a pressure of 1 to 5 atmospheres is injected by means of a conventional diffuser 126 such as a perforated plate or a porous plate for a reaction time of 1 to 120 minutes in order to dissolve the carbon dioxide and to form carbonic acid, The carbonic acid continuously reacts with the lithium carbonate to form the more soluble lithium bicarbonate according to reaction (7), until reaching a lithium bicarbonate concentration in solution of 1 to 58 g/L.

[0039] Once the capacity of dissolution of lithium bicarbonate (saturation value) of the solution is reached, for example 52g.L at 15°C, the solution containing the lithium

bicarbonate 107 is filtered in a conventional filter 108 i.e. a press filter to remove insoluble impurities 109 which can be discarded.

[0040] The filtrate 110 containing lithium bicarbonate is continuously accumulated in a conventional holding tank 111. Once the solution 107 has been filtered, the filtered
5 solution 112 is transferred from the tank 111 back into to the reactor 102. Steam or other heating media is added through a conventional heat exchanger 113 located inside the reactor 102 for 1 to 120 minutes to heat the solution of lithium bicarbonate to a temperature of 50 to 100°C in order to decompose the lithium bicarbonate back to lithium carbonate according to reaction (8), since lithium bicarbonate is unstable above 50°C,
10 decomposing and generating carbon dioxide and precipitating lithium carbonate. The pressure of the gas in the reactor 102 is maintained at 0.1 to 5 atmospheres.

[0041] The pulp 115 is maintained at a temperature of 50 to 95°C and filtered at 50 to 95°C in a conventional filter 116 e.g. a press filter, where the lithium carbonate cake is washed with two volumes of demineralized water 127 at a temperature of 50 to 95°C.
15 Both the filtrate and wash water filtrate 117 are sent to solar evaporation ponds to concentrate the solution for further lithium recovery. The purified lithium carbonate cake 118 is sent to a drying step at a temperature of 150 to 200°C for a drying time of 1 to 120 minutes in a conventional indirect heated dryer (not shown).

[0042] The carbon dioxide gas 128 generated in the decomposition step of the
20 lithium bicarbonate in the reactor 102 passes through a conventional condenser 119 with water cooling 120 or other cooling agent in order to condense the water generated by vaporization of the water and the water generated in the decomposition of the lithium bicarbonate according to reaction (8). The condensed water 121 can be discarded, and the cooled carbon dioxide 122 can be recirculated back into the pressurized tank 123.
25 Additional water trapped in the gas 125 can be drained periodically from the tank 123. Additional carbon dioxide 140 can be added to maintain the required mass balance and to compensate for gas losses.

[0043] The following is an example of the process of the present invention.

EXAMPLE

[0044] A solar concentrated brine from Salar de Cauchari, Argentina, with the chemical composition given in Table 5 was treated with a solution saturated in lime
5 (Ca(OH)₂) to maintain a pH of 11 at 10°C for a time span of 30 minutes.

Table 5. Chemical composition of concentrated brine from Salar de Cauchari.

Element	Li	Cl	Na	K	Ca	Mg	SO₄⁼	B	H₂O
wt-%	0.410	12.810	5.423	2.721	2.482	9.931	5.936	0.445	55.423

[0045] The treated brine was sent to a solar evaporation pond where mostly Mg(OH)₂, CaSO₄·5H₂O and CaB₂O₄·6H₂O salts were crystallized. The resulting brine had
10 the composition shown in Table 6.

Table 6. Chemical composition of brine treated by liming from Salar de Cauchari..

Element	Li	Cl	Na	K	Ca	Mg	SO₄⁼	B	H₂O
wt-%	0.719	14.220	2.856	4.199	0.016	0.008	2.967	0.698	74.183

[0046] The brine described in Table 6, with a boron content of 0.698 wt-% and a
15 pH 10.2, was acidulated with hydrochloric acid of 25 wt-% concentration to lower the pH to 4. The brine then was treated by solvent extraction utilizing as extractant 85% in volume of iso-octylic alcohol with 15% in volume of tributyl-phosphate as phase modifier dissolved in the commercial aromatic solvent Escaid™ 110 in a proportion of 20% in volume of the extractant and 80% in volume of the solvent.

[0047] The brine was treated in four extraction stages using an organic:brine ratio
20 of 4:1 for a contact time of 4 minutes in each stage and a settling time of 15 minutes in each stage. The resulting brine after boron extraction contained 0.004 wt-% of residual boron.

[0048] The charged organic extractant was further treated with an alkaline solution of 0.25 molar of sodium hydroxide with an organic:aqueous ratio of 3:1 in three re-extraction stages with a re-extraction time of 5 minutes and a settling time of 8 minutes per stage. The alkaline solution with 1.36 wt-% boron was sent to the solar evaporation ponds,
5 and the boron-depleted extractant was recirculated back to the process.

[0049] The boron-free brine was then treated with a solution of 25 wt-% soda ash maintaining a pH of 10.5 and a temperature of 90-95°C for a reaction time of 50 minutes. The pulp generated was hot thickened at 85-90°C and the dense pulp produced was hot filtered in a press filter at 80-85°C. The lithium carbonate cake obtained was washed in
10 the filter with two volumes of demineralized water at 95°C.

[0050] The filtrate was sent to a solar evaporation pond and the lithium carbonate cake was fed continuously through a rotating sealing star valve into a closed agitated vessel filled with demineralized water at 10°C, where carbon dioxide from a pressure tank was bubbled continuously through a metallic diffuser at the bottom of the vessel to form
15 carbonic acid. The total pressure inside the vessel was 1.5 atmospheres and the process was maintained in operation under these conditions until the lithium bicarbonate level in the solution reached a value of 52 g/L.

[0051] The solution containing the lithium bicarbonate was then filtered in a press filter. The clear filtrate was continuously accumulated in a holding tank. Once the
20 solution of lithium bicarbonate was filtered, it was pumped back into the reaction vessel where steam was passed through a heat exchanger to heat the lithium bicarbonate solution to 95°C, agitating the liquid at 50 RPM continuously. Once this temperature was reached, the solution was maintained at 95°C for 30 minutes with agitation. The steam and carbon dioxide generated was sent to a tube condenser to condense and separate the water from
25 the CO₂ which was pumped back into the CO₂ pressure tank.

[0052] The pulp containing the purified lithium carbonate was hot thickened at 85-90°C and the dense pulp obtained was filtered in a filter press at 80-85°C. The cake of

purified lithium carbonate was washed with two volumes of demineralized water at 95°C. The filtrate was sent to a solar evaporation pond. The purified lithium carbonate was dried at 200°C for 35 minutes in an indirectly heated dryer.

[0053] The dry high purity battery-grade lithium carbonate produced had the
5 chemical analysis shown in Table 7.

Table 7. Purified battery-grade lithium carbonate produced.

Element	Li	Li₂CO₃	Na	K	Cl	Mg	Ca	B
wt-%	18.71	99.51	0.00003	0.00001	0.002	0.0004	0.001	0.0003

[0054] The above description is exemplary of the process of the invention and may
be varied. Such variations are not to be regarded as a departure from the spirit and scope
10 of the invention, and all such modifications are intended to be included within the scope of
the following claims.

CLAIMS

1. A process for producing high purity battery-grade lithium carbonate from a natural or industrial brine containing lithium, which comprises:
- 5 (a) adding a calcium hydroxide solution to the brine to precipitate magnesium, calcium and boron in the brine, and removing precipitated magnesium, calcium and boron to produce a treated brine;
 - (b) solar concentrating the treated brine to precipitate and separate magnesium, calcium and boron and to produce a magnesium - free brine;
 - 10 (c) subjecting said magnesium-free brine to a solvent extraction with an organic extractant for removal of boron to thereby produce a boron-free brine;
 - (d) adding sodium carbonate to said boron-free brine to precipitate lithium carbonate;
 - 15 (e) separating said lithium carbonate from said brine to thereby obtain a lithium carbonate cake;
 - (f) dissolving the lithium carbonate cake in water and injecting gaseous carbon dioxide into the water to form a lithium bicarbonate solution;
 - (g) separating insoluble impurities contained in said lithium carbonate from the lithium bicarbonate solution;
 - 20 (h) heating the solution of lithium bicarbonate to decompose said lithium bicarbonate to precipitate purified lithium carbonate;
 - (i) separating said purified lithium carbonate from said solution; and
 - (j) drying said purified lithium carbonate.

2. The process according to claim 1, wherein the magnesium, calcium and boron in step (b) are precipitated as magnesium hydroxide, pentahydrated calcium sulfate and heptahydrated calcium borate and wherein said magnesium - free brine contains 0.8-1.2 wt-% lithium and less than 0.001 wt-% magnesium.
- 5 3. The process according to claim 1, wherein the organic extractant in solvent extraction in step (c) is an aliphatic alcohol organic extractant dissolved in an aromatic solvent in a organic:brine ratio of 1:5 to 6:1, for a total contact time of 1 to 60 minutes and a total settling time of 1 to 120 minutes at a temperature of 0 to 50°C and a pH of 1 to 7 in one or more stages of extraction and adding tributylphosphate in 5 to 20% volume with
10 respect to the organic extractant as a phase modifier, and re-extracting the boron from the loaded organic in one or more re-extraction stages with an aqueous solution of sodium hydroxide of 0.01 to 3 mol/l for a total contact time of 1 to 60 minutes and a total settling time of 1 to 120 minutes at a temperature of 0 to 50°C to produce a boron - free brine.
4. The process according to claim 1 or 2, wherein said boron-free brine in step (d) is
15 heated to a temperature of 70 to 100°C before adding sodium carbonate as an aqueous solution of 20 to 30 wt-% sodium carbonate at a pH of 8 to 12 for reaction with the brine at the temperature of 70 to 100°C for a reaction time of 5 to 150 minutes in one or more stages to precipitate lithium carbonate.
5. The process according to any one of claims 1, 2 or 3 wherein the lithium carbonate
20 precipitate is separated from the brine in step (e) by thickening and filtering the precipitate at a temperature between 50 to 95°C to produce a lithium carbonate cake.
6. The process according to any one of claims 1 to 5, wherein said lithium carbonate
cake in step (f) is reacted with an aqueous saturated solution of carbonic acid generated by dissolving carbon dioxide at a pressure of 1 to 5 atmospheres in demineralized water at a
25 temperature of 0 to 30°C for a reaction time of 1 to 120 minutes to form lithium bicarbonate in solution with a concentration of 1 to 58 g/L.

7. The process according to any one of claims 1 to 6, wherein said lithium bicarbonate solution in step (g) is filtered in a press filter to separate insoluble impurities from said lithium bicarbonate in solution.
8. The process according to any one of claims 1 to 7, wherein said filtered lithium bicarbonate solution in step (h) is heated at 50 to 100°C for a reaction time of 1 to 120 minutes at a total pressure of 0.1 to 5 atmospheres to decompose the lithium bicarbonate and to generate a purified lithium carbonate and gaseous carbon dioxide.
9. The process according to any one of claims 1 to 8, wherein the purified lithium carbonate is separated from the solution in step (i) by thickening and filtering the lithium carbonate at a temperature between 50 to 95°C to produce a purified lithium carbonate cake which is washed with one or more volumes of demineralized water at a temperature of 50 to 95°C.
10. The process according to any one of claims 1 to 9, wherein said purified lithium carbonate in step (j) is dried in an indirect dryer at 100-250°C for a drying time of 1 to 120 minutes.
11. The process according to claim 3, wherein a solution containing the boron from the re-extraction stage is send to solar evaporation ponds.
12. The process according to claim 5, wherein a filtrate and wash water filtrate in step (e) are send to solar evaporation ponds.
13. The process according to claim 8, wherein the gaseous carbon dioxide generated in step (h) is recirculated to the process in step (f).
14. The process according to claim 9, wherein a filtrate and wash water filtrate in step (i) are send to solar evaporation ponds.

Figure 1:

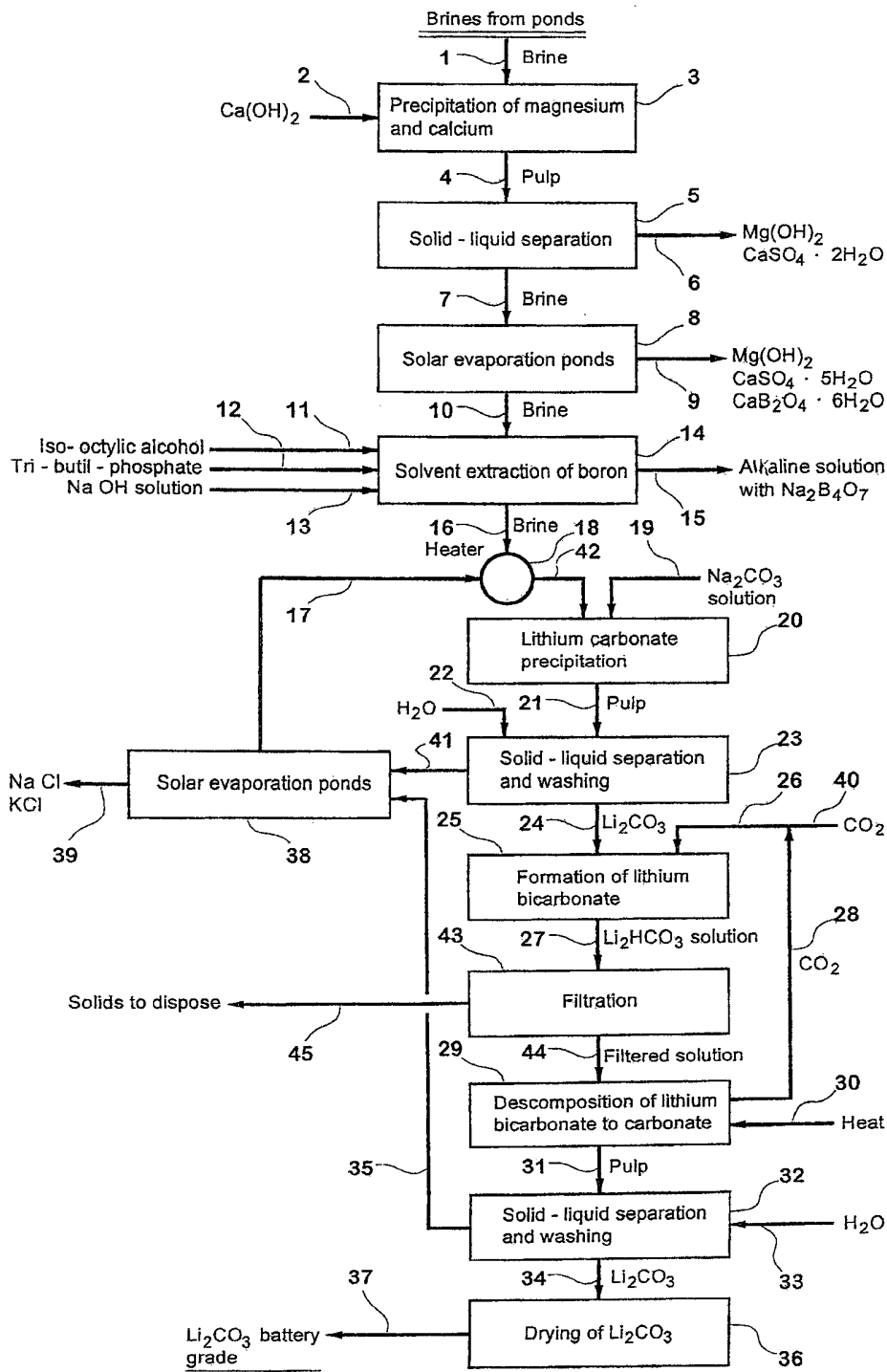


Figure 2

