A process (10) for the production of lithium carbonate, the process characterised by the steps of: (i) Calcining (20) an alpha-spodumene ore or concentrate (12) to produce beta-spodumene; (ii) Sulphating (28) the beta-spodumene at elevated temperature; (iii) Passing the sulphated beta-spodumene to a leach step (30) in which lithium sulphate is leached in water; (iv) Passing the pregnant leach solution from the leach step to a series of impurity removal steps in which iron, alumina, silicates and magnesium are, in large part, precipitated and removed (34, 36 and 38); (v) Adding sodium carbonate (42) to the product of step (iv) by which calcium is precipitated (40); (vi) The product of step (v) is then passed to an ion exchange step (50) in which residual calcium, magnesium and other remaining multivalent cations are substantially removed; and (vii) Passing the purified product of step (vi) to a lithium carbonate precipitation step (56) in which sodium carbonate (54) is added to produce precipitated lithium carbonate and a sodium sulphate mother liquor.
"Process for the Production of Lithium Carbonate"

Field of the Invention

The present invention relates to a process for the production of lithium carbonate. More particularly, the process of the present invention is intended to provide a high purity or battery grade lithium carbonate product. The process of the present invention may also provide a sodium sulphate product.

Background Art

Known processes for the production of lithium carbonate from lithium containing ores or concentrates typically utilise the thermal treatment of an alpha-spodumene ore or concentrate. This thermal treatment can be referred as decrepitation and transforms the alpha-spodumene to beta-spodumene which is in turn able to be solubilised by acid. The step in which the beta-spodumene is sulphated in acid takes place in a kiln and produces water soluble lithium sulphate. The lithium sulphate is passed to one or more leaching tanks in which the lithium sulphate is leached with water. Limestone, lime and sodium carbonate are subsequently added to the product of the leach so as to adjust the pH of the slurry, whereby certain impurities, including iron, aluminium, magnesium and calcium are precipitated. The residue is then separated which leaves a concentrated solution of lithium sulphate. The lithium sulphate solution is then treated with a concentrated sodium carbonate solution so as to precipitate lithium carbonate. Such a process is described in Canadian Patent 1297265.

However, the above described process of the prior art is relatively inefficient in the removal of impurities that remain in the pregnant leach solution, which results in a relatively impure lithium carbonate product. This is particularly problematic when attempting to produce a high quality or battery grade lithium carbonate product.

Further, the lithium carbonate precipitation step of the prior art results in a sodium sulphate solution in addition to the precipitated lithium carbonate. The sodium sulphate solution has traditionally been treated to crystallise sodium sulphate decahydrate for drying and disposal or sale, with some liquor recirculated to the
water leach of the lithium sulphate. Such a process does not effectively utilise the sodium sulphate solution to produce a sodium sulphate product, the sodium decahydrate requiring drying/or heating before disposal. Similarly, the impurities removed from the pregnant leach solution, including iron, alumina and silicates have simply passed to waste and have remained unutilised.

Attempts have been made previously to increase the purity of lithium carbonate product, particularly that obtained from brines or bitterns. Such efforts include the use of carbon dioxide to produce a lithium bicarbonate solution, at elevated pressure (up to 20 atm), with the subsequent precipitation of lithium carbonate. An additional further purification step is then necessary, such as a further ion exchange or separation step, to produce the target purity of lithium carbonate. Such a process is described in US Patent 6048507 to Amouzegar et al. The need in such processes for elevated pressure and additional impurity removal steps impacts adversely on the economy of the process.

The process of the present invention has as one object thereof to overcome substantially one or more of the above mentioned problems associated with prior art processes, or to at least provide a useful alternative thereto.

Each document, reference, patent application or patent cited in this text is expressly incorporated herein in their entirely by reference, which means that it should be read and considered by the reader as part of this text. That the document, reference, patent application, or patent cited in this text is not repeated in full in this text is merely for reasons of brevity.

Reference to cited material or information contained in the text should not be understood as a concession that the material or information was part of the common general knowledge or was known in Australia or any other country.

Throughout this specification, unless the context requires otherwise, the word "comprise", or variations such as "comprises" or "comprising", will be understood to imply the inclusion of a stated integer or group of integers but not the exclusion of any other integer or group of integers.
Disclosure of the Invention

In accordance with the present invention there is provided a process for the production of lithium carbonate, the process characterised by the steps of:

(i) Calcining an alpha-spodumene ore or concentrate to produce beta-spodumene;

(ii) Sulphating the beta-spodumene at elevated temperature;

(iii) Passing the sulphated beta-spodumene to a leach step in which lithium sulphate is leached in water;

(iv) Passing the pregnant leach solution from the leach step to a series of impurity removal steps in which iron, alumina, silicates and magnesium are, in large part, precipitated and removed;

(v) Adding sodium carbonate to the product of step (iv) by which calcium is precipitated;

(vi) The product of step (v) is then passed to an ion exchange step in which residual calcium, magnesium and other remaining multivalent cations are substantially removed; and

(vii) Passing the purified product of step (vi) to a lithium carbonate precipitation step in which sodium carbonate is added to produce precipitated lithium carbonate and a sodium sulphate mother liquor.

Preferably, the mother liquor from step (vii) is passed to an anhydrous sodium sulphate recovery process from which a solid sodium sulphate product is obtained. A portion of the sodium sulphate mother liquor is preferably recirculated to the leach of step (iii).

The lithium carbonate precipitation step (vii) is preferably conducted in at least one draft tube baffled crystalliser with a residence time of about 90 minutes.
Preferably, the lithium carbonate precipitation step (vii) is conducted sequentially in two crystallisers.

In one form of the invention the precipitated lithium carbonate of step (vii) is thickened prior to passing to a filter step. The filter step is preferably followed by a repulp washing stage and a centrifuge step. Both the filter step and centrifuge step preferably incorporate a hot wash to reduce impurities. The resulting product is preferably then milled to minus 6 µm.

In another form of the present invention the precipitated lithium carbonate of step (vii) is thickened prior to passing to a bicarbonate circuit, the bicarbonate circuit comprising digestion with carbon dioxide to produce a bicarbonate intermediate, and subsequent crystallisation to produce a lithium carbonate product of increased purity.

Preferably, the sodium sulphate recovery process is fed from the thickening step after the lithium carbonate precipitation step (vii). The sodium sulphate recovery process preferably comprises creating a supersaturated solution and passing this solution to a crystallisation step. The crystallisation step is preferably conducted at a temperature of about 80°C to 90°C and a pressure of about 45 kPa(a). The residence time is preferably about 60 minutes.

Still preferably, water evaporated from the solution in the creation of the supersaturated solution is recompressed, combined with make-up steam and utilised in the anhydrous sodium sulphate crystallisation step. This crystallisation step preferably utilises a vacuum evaporative crystalliser.

The crystallisation step produces a crystal slurry that is preferably discharged to a centrifuge step. This centrifuge step preferably further comprises a wash with water, the liquid product of which is recycled back to the leach step (iii). The solid product of the centrifuge step and wash is then preferably dried.

Preferably, the impurity removal steps of step (iv) comprise, in turn, the addition of lime/hydrated lime, hydrogen peroxide and sodium hydroxide. After the addition of the hydrogen peroxide the slurry is preferably thickened, the underflow of the
thickening step then being filtered and dried to provide an alumina silicate product.

Still preferably, the beta-spodumene of step (i) is cooled and milled prior to the sulphating step (ii). The beta-spodumene is preferably milled to less than about 300 μm.

Still further preferably, the sulphating step (ii) is conducted in a sulphating kiln at about 250°C over a residence time of about 45 minutes.

Still further preferably, the sulphated spodumene is cooled prior to feeding into the leach step (iii).

The bicarbonate circuit preferably further comprises a centrifuge/wash step and a repulp step prior to the digestion step. The digestion step is preferably conducted at atmospheric pressure and at a temperature of less than about 20°C to 40°C.

Preferably, the crystallisation step comprises the addition of steam to a lithium bicarbonate product of the digestion step, thereby producing both carbon dioxide and lithium carbonate products. The crystallisation step is preferably conducted at about 95°C.

Still preferably, the lithium carbonate product of the crystallisation step is passed to a thickening step, the overflow from which is passed, at least in part, to the repulp step prior to the digestion step. The overflow is preferably subjected to cooling prior to passing to the repulp step.

In a preferred form of the present invention a lithium carbonate product of the thickening step provided after the crystallisation step is passed, or recirculated, to a point in the bicarbonate circuit prior to the digestion step so as to increase the purity of the ultimate lithium carbonate product. Preferably, the recirculated lithium carbonate is added to the centrifuge step prior to the repulp step.

In accordance with the present invention there is further provided a process for the production of lithium carbonate, the process characterised by the steps of:
(i) Calcining an alpha-spodumene or ore concentrate to produce beta-
spodumene;

(ii) Sulphating the beta-spodumene at elevated temperature;

(iii) Passing the sulphated beta-spodumene to a leach step in which
lithium sulphate is leached in water;

(iv) Passing the pregnant leach solution from the leach step to a series
of impurity removal steps in which iron, alumina, silicates and
magnesium are, in large part, precipitated and removed;

(v) Adding sodium carbonate to the product of step (iv) by which
calcium is precipitated;

(vi) The product of step (v) is then passed to an ion exchange step in
which residual calcium, magnesium and other remaining multivalent
cations are substantially removed;

(vii) Passing the purified product of step (vi) to a lithium carbonate
precipitation step in which sodium carbonate is added to produce
precipitated lithium carbonate and a sodium sulphate mother liquor;
and

(viii) Passing the precipitated lithium carbonate of step (vii) to a
bicarbonate circuit, the bicarbonate circuit comprising digestion with
carbon dioxide to produce a bicarbonate intermediate, and
subsequent crystallisation to produce a lithium carbonate product of
increased purity.

Brief Description of the Drawings

The process of the present invention will now be described, by way of example
only, with reference to two embodiments thereof and the accompanying drawings,
in which:-
Figure 1 is a schematic flow-sheet depicting a process for the production of lithium carbonate in accordance with a first embodiment of the present invention; and

Figure 2 is a schematic flow-sheet depicting a bicarbonate circuit that is provided as a substitute for a portion of the process of Figure 1, in accordance with a second embodiment of the present invention.

Best Mode(s) for Carrying Out the Invention

In Figure 1 there is shown a process 10 for the production of lithium carbonate, in accordance with a first embodiment of the present invention.

All of the unit operations embodied in the process 10 are designed to operate continuously with full process instrumentation and control being provided for.

A concentrate stockpile and reclaim area 12 encompasses a 12 week capacity stockpile (30,000T) of alpha-spodumene concentrate 14. Front end loaders 16 and belt conveyors 18 transport the alpha-spodumene concentrate to a calcining step, conducted in a direct fired rotary kiln calciner 20.

The alpha-spodumene concentrate is calcined at about 1080°C to convert the alpha-spodumene to the teachable beta-spodumène. Off-gases from the calciner 20 are directed through a cyclone and an electrostatic precipitator specified to comply with known environmental emissions limits. The hot calcine is indirectly cooled in a cooling step 22 and then dry-milled to less than 300 μm in a ball mill 24.

After storage in a surge bin, the beta-spodumene is mixed with a 40% excess of concentrated (98% w/w acid) sulphuric acid 26, and roasted at 250°C for about 30 to 45 minutes in an indirectly heated sulphating kiln 28. Off-gases from the sulphating kiln 28 are cleaned in a wet scrubber. The sulphated beta-spodumene is then cooled to 95°C in a bin that feeds a leach circuit 30. An excess of at least 20% acid (based on the lithium content of the ore), preferably at least 40% acid, is used to maximise the lithium extraction while minimising reagent use and any need for sulphate addition to the leach circuit 30.
The spodumene is leached in the leach circuit 30 in a recycled sodium sulphate solution 32. The leach circuit 30 comprises a few leaching tanks operating at about 60°C to 80°C. About 95% of the lithium is leached from the beta-spodumene. Soluble iron, aluminium and magnesium are removed in large part from the leach liquor through a series of impurity removal steps, including pH modification (raising) through the addition of hydrated lime 34, the addition of hydrogen peroxide 36 (to ensure iron is present in the ferric form), and precipitation of magnesium through the addition of hydrated lime 38 at a pH of about 10. Calcium is then removed in a calcium precipitation step 40 with the addition of sodium carbonate 42. The impurity precipitation occurs with the leached solids present in the slurry.

A thickening step 44 is provided prior to the addition of the hydrated lime 38. The overflow from the thickening step 44 is passed to a filter step, for example a polishing sand filter 46. The underflow from both the thickening step 44 and the filter 46 are passed to a filter step to be described hereinafter.

The product of the calcium precipitation step 40 is passed to a filtration step comprising a polishing filter 47. A resulting filtrate 48 is passed through a polishing sand filter 47 and an ion exchange step 50, comprising an IX column 50 to remove residual calcium, magnesium and other multivalent cations.

The solution passing from the ion exchange step 50 is heated 52 and then reacted with a hot sodium carbonate solution 54 in a lithium carbonate crystalliser 56 operating at 85°C. The crystalliser 56 is a draft tube baffled crystalliser and the solution flashed therein is highly supersaturated. A secondary crystalliser 56 is also provided, to which the supersaturated solution is passed after the first crystalliser 56 so as to remove the super-saturation. The result is small, inclusion-free crystals of lithium carbonate readily amenable to milling.

The small crystals from the crystalliser 56 are thickened in a thickening step 58 before passing to a filter step, incorporating for example a belt filter 60. The filter step 60 is followed by a repulp washing stage 62 (at 40% w/w solids) before the crystals are sent to a continuous centrifuge 66. To reduce impurities, for example residual entrained sodium sulphate, the filter step 60 and the centrifuge 66 use a
hot wash 68, achieving an overall wash efficiency of 99%.

Solid crystals resulting from the centrifuge 66 are dried in an indirect-fired kiln 70 at 120°C. Resulting dry coarse lithium carbonate is air milled to less than 6 µm in a micronizer 72 and then pneumatically conveyed to storage bins, cooled to 50°C in a jacketed screw conveyer and then bagged 74.

The majority of the overflow from the thickening step 58 passes to a sodium sulphate precipitation step 76. The remainder of the flow is recycled to the leach circuit 30. The sodium sulphate in solution, about 293 gpl, is precipitated or crystallised in, for example, a vacuum evaporative crystalliser operating at a temperature of about 80°C to 90°C and pressure of about 45 kPa(a). This allows the use of lower cost materials of construction for the crystalliser. The residence time is about 60 minutes so as to achieve a coarse crystal product. Supersaturation is achieved in the precipitation step 76 by evaporating approximately half the water from the overflow of the thickening step 58 in the evaporative crystallisation stage. The resulting water vapour is recompressed, combined with make-up steam 78 and used as the evaporative medium for the crystalliser.

A crystal slurry 80 is discharged to a single continuous centrifuge 82, where crystals are washed by cold water 84 achieving a wash efficiency of 99%. The resulting solution 32 is recycled back to the leach circuit 30. Solids from the centrifuge 82 are fed to an indirect-fired kiln 86, operating at about 120°C, which dries the crystals. The crystal product is pneumatically conveyed to product bins 88, and cooled to less than 80°C in a jacketed screw conveyer as it is conveyed from the bins to bagging stations.

Condensate throughout the process 10 is used as make-up water for hot process water, cold process water and cooling water. As the process 10 does not return condensate there is an overall positive water balance and about 1 t/h of process water is discharged to a waste (not shown).

It is to be understood that the thickening step 58 may be bypassed with certain draft tube baffled crystalliser designs.
It is further envisaged that tantalite and alumina may also be recovered using the process 10 of the present invention. The filter cake from the thickening step 44 may be discharged to a tantalite recovery plant (not shown). Discharge from the tantalite recovery plant may be fed onto a belt filter to remove water, which is returned to the tantalite recovery plant. The filter does not use washing and has a filtration area of 19 m². The filter cake from the belt filter is dried in a direct-fired kiln. The dry alumina silicate is cooled to 50°C in a jacketed screw conveyor and then pneumatically conveyed to a storage bin prior to dispatch.

In Figure 2 there is shown a bicarbonate circuit 100 in accordance with a second embodiment of the present invention. The bicarbonate circuit 100 is intended for use in combination with a significant proportion of the process 10 of the first embodiment of the present invention and reference to like numerals denotes like parts or steps. However, this should not be understood to limit the generality of use of the bicarbonate circuit 100 as it is envisaged that the bicarbonate circuit 100 may have applications beyond that exemplified herein.

In the second embodiment of the present invention the small crystals from the crystalliser 56 that are thickened in the thickening step 58 are, rather than being passed to the belt filter 60 of Figure 1, passed to the bicarbonate circuit 100 of Figure 2.

Underflow from the thickening step 58 is passed, at a temperature of about 85°C, to a centrifuge 102 in which the lithium carbonate crystals are washed. The lithium carbonate product is about 99.0% purity at this point. The product of the centrifuge 102 has a moisture content of about 14% and is directed to a repulp step 104 to which a cooled recirculation liquor 108, to be described hereinafter, is added. The temperature of the repulp step 104 is about 45°C.

The product of the repulp step 104 is about 2 to 5% w/w solids which are directed to a digestion step 110 at less than about 50°C, for example 40°C. The digestion step 110 comprises the addition of a carbon dioxide feed stream 112 to the repulped lithium carbonate from the repulp step 104, with the addition of cooling, in a stirred reactor vessel at atmospheric pressure for a time of about 90 minutes, producing a lithium bicarbonate intermediate product 114 at less than about 50°C,
for example 40°C.

The lithium bicarbonate intermediate product 114 is passed from the digestion step 110 to a filter step 116. A filter bypass route 118 is available. The lithium bicarbonate intermediate product 14 is in turn passed to a crystallisation step 120 comprising a multi-compartment agitated reactor vessel to which a steam feed 122 added. The crystallisation step 120 is conducted at atmospheric pressure in three overflow stages at about 95°C, and produces lithium carbonate crystals 124 and carbon dioxide 126 products.

The carbon dioxide product 126 from the crystallisation step 120 is compressed 128, passed to a drying step 130 using a condenser, and produces a condensate 106 as a product. This condensate 106 is combined with an overflow from a thickener 136, to be described hereinafter. From the drying step 130 the carbon dioxide is passed to further compression 132. At least a portion of the carbon dioxide from the compression step 132 is utilised as the carbon dioxide 112 for use in the digestion step 110. Any excess carbon dioxide from compression may be stored in tank(s) 134. Alternatively, carbon dioxide may also be drawn from tanks 134 for use in the digestion step 134.

The lithium carbonate product 124 of the crystallisation step 120 is passed, at about 95°C, to a thickening step 136, from which the overflow 138 is recirculated either as the recirculation liquor 108 after a cooling step(s) 142, to the repulp step 104, or as a bleed 144 to the leach circuit 30 shown in Figure 1. The cooling of the recirculation liquor 108 in the cooling step(s) 142, which may incorporate a chiller 146, reduces the temperature from about an initial 94°C to about 35°C prior to addition to the repulp step 104.

Lithium carbonate underflow 148 from the thickening step 136 is passed to a centrifuge 150 in which it is washed, with the subsequent lithium carbonate product then being passed to a dryer 70 as shown in Figure 1, and the subsequent steps as described with reference to that Figure. The lithium carbonate product so produced is about 99.9% purity, or battery grade.

Additional purification may be achieved through a recycle 152 of all, or a portion
of, the lithium carbonate product from the centrifuge step 150 to the centrifuge step 102. This can be expected to increase the purity of the ultimate lithium carbonate product to a target of above 99.9% purity.

Any available low grade lithium carbonate 154 may be fed to the repulp step 104 to be repulped, and purified via the bicarbonate circuit 100.

It is envisaged that the bicarbonate circuit 100 may be by-passed should maintenance be required. The lithium carbonate product so produced will be an "off-spec" material, typically of technical grade.

Overall lithium recovery through the process of the present invention is about 82%.

As can be seen from the above, the process of the present invention provides a process by which a high purity or battery grade lithium carbonate product may be obtained from an alpha-spodumene ore or concentrate. The purity of the lithium carbonate product may be improved further through incorporation of a bicarbonate circuit as described. Further, the process of the present invention also allows the production of a useful sodium sulphate product. The process of the present invention as described herein is typically a simpler and more economic route to the production of a high purity lithium carbonate product when compared with processes that have been described in the prior art.

Modifications and variations such as would be apparent to the skilled addressee are considered to fall within the scope of the present invention.
Claims:

1. A process for the production of lithium carbonate, the process characterised by the steps of:
   
   (i) Calcining an alpha-spodumene ore or concentrate to produce beta-spodumene;
   
   (ii) Sulphating the beta-spodumene at elevated temperature;
   
   (iii) Passing the sulphated beta-spodumene to a leach step in which lithium sulphate is leached in water;
   
   (iv) Passing the pregnant leach solution from the leach step to a series of impurity removal steps in which iron, alumina, silicates and magnesium are, in large part, precipitated and removed;
   
   (v) Adding sodium carbonate to the product of step (iv) by which calcium is precipitated;
   
   (vi) The product of step (v) is then passed to an ion exchange step in which residual calcium, magnesium and other remaining multivalent cations are substantially removed; and
   
   (vii) Passing the purified product of step (vi) to a lithium carbonate precipitation step in which sodium carbonate is added to produce precipitated lithium carbonate and a sodium sulphate mother liquor.

2. A process according to claim 1, wherein the mother liquor from step (vii) is passed to an anhydrous sodium sulphate recovery process from which a solid sodium sulphate product is obtained.

3. A process according to claim 1 or 2, wherein a portion of the sodium sulphate mother liquor is also recirculated to the leach of step (iii).
4. A process according to any one of the preceding claims, wherein the lithium carbonate precipitation step (vii) is preferably conducted in at least one draft tube baffled crystalliser with a residence time of about 90 minutes.

5. A process according to claim 4, wherein the lithium carbonate precipitation step (vii) is conducted sequentially in two crystallisers.

6. A process according to any one of the preceding claims, wherein the precipitated lithium carbonate of step (vii) is thickened prior to passing to a filter step.

7. A process according to claim 6, wherein the filter step is followed by a repulp washing stage and a centrifuge step.

8. A process according to claim 7, wherein both the filter step and centrifuge step incorporate a hot wash to reduce impurities.

9. A process according to claim 7 or 8, wherein the product of the centrifuge step is subsequently milled to minus 6 \( \mu \text{m} \).

10. A process according to any one of the preceding claims, wherein the precipitated lithium carbonate of step (vii) is thickened prior to passing to a bicarbonate circuit, the bicarbonate circuit comprising digestion with carbon dioxide to produce a bicarbonate intermediate, and subsequent crystallisation to produce a lithium carbonate product of increased purity.

11. A process according to any one of claims 2 to 10, wherein the sodium sulphate recovery process is fed from the thickening step after the lithium carbonate precipitation step (vii).

12. A process according to claim 11, wherein the sodium sulphate recovery process comprises creating a supersaturated solution and passing this solution to a crystallisation step.
13. A process according to claim 12, wherein the crystallisation step is conducted at a temperature of about 80°C to 90°C and a pressure of about 45 kPa(a).

14. A process according to claim 12 or 13, wherein the crystallisation step has a residence time of about 60 minutes.

15. A process according to any one of claims 12 to 14, wherein water evaporated from the solution in the creation of the supersaturated solution is recompressed, combined with make-up steam and utilised in the anhydrous sodium sulphate crystallisation step.

16. A process according to any one of claims 12 to 15, wherein the crystallisation step utilises a vacuum evaporative crystalliser.

17. A process according to any one of claims 12 to 16, wherein the crystallisation step produces a crystal slurry that is discharged to a centrifuge step.

18. A process according to claim 17, wherein the centrifuge step further comprises a wash with water, the liquid product of which is recycled back to the leach step (iii).

19. A process according to claim 18, wherein the solid product of the centrifuge step and wash is then dried.

20. A process according to any one of the preceding claims, wherein the impurity removal steps of step (iv) comprise, in turn, the addition of lime/hydrated lime, hydrogen peroxide and sodium hydroxide.

21. A process according to claim 20, wherein after the addition of the hydrogen peroxide the slurry is thickened, an underflow of the thickening step then being filtered and dried to provide an alumina silicate product.

22. A process according to any one of the preceding claims, wherein the beta-spodumene of step (i) is cooled and milled prior to the sulphating step (ii).
23. A process according to claim 22, wherein the beta-spodumene is milled to less than about 300 µm.

24. A process according to any one of the preceding claims, wherein the sulphating step (ii) is conducted in a sulphating kiln at about 250°C over a residence time of about 45 minutes.

25. A process according to claim 24, wherein the sulphated spodumene is cooled prior to feeding into the leach step (iii).

26. A process according to any one of claims 10 to 25, wherein the bicarbonate circuit further comprises a centrifuge/wash step and a repulp step prior to the digestion step.

27. A process according to any one of claims 10 to 26, wherein the digestion step is conducted at atmospheric pressure and at a temperature of less than about 20°C to 40°C.

28. A process according to any one of claims 10 to 27, wherein the crystallisation step comprises the addition of steam to a lithium bicarbonate product of the digestion step, thereby producing both carbon dioxide and lithium carbonate products.

29. A process according to any one of claims 10 to 28, the crystallisation step is conducted at about 95°C.

30. A process according any one of claims 10 to 29, the lithium carbonate product of the crystallisation step is passed to a thickening step, the overflow from which is passed, at least in part, to the repulp step prior to the digestion step.

31. A process according to claim 30, the overflow is subjected to cooling prior to passing to the repulp step.

32. A process according to claim 30 or 31, wherein a lithium carbonate product of the thickening step provided after the crystallisation step is passed, or
recirculated, to a point in the bicarbonate circuit prior to the digestion step so as to increase the purity of the ultimate lithium carbonate product.

33. A process according to claim 32, wherein the recirculated lithium carbonate is added to the centrifuge step prior to the repulp step.

34. A process for the production of lithium carbonate, the process characterised by the steps of:

(i) Calcining an alpha-spodumene or ore concentrate to produce beta-spodumene;

(ii) Sulphating the beta-spodumene at elevated temperature;

(iii) Passing the sulphated beta-spodumene to a leach step in which lithium sulphate is leached in water;

(iv) Passing the pregnant leach solution from the leach step to a series of impurity removal steps in which iron, alumina, silicates and magnesium are, in large part, precipitated and removed;

(v) Adding sodium carbonate to the product of step (iv) by which calcium is precipitated;

(vi) The product of step (v) is then passed to an ion exchange step in which residual calcium, magnesium and other remaining multivalent cations are substantially removed;

(vii) Passing the purified product of step (vi) to a lithium carbonate precipitation step in which sodium carbonate is added to produce precipitated lithium carbonate and a sodium sulphate mother liquor; and

(viii) Passing the precipitated lithium carbonate of step (vii) to a bicarbonate circuit, the bicarbonate circuit comprising digestion with carbon dioxide.
to produce a bicarbonate intermediate, and subsequent crystallisation to produce a lithium carbonate product of increased purity.

35. A process for the production of lithium carbonate substantially as hereinbefore described with reference to Figure 1 or 2.
**INTERNATIONAL SEARCH REPORT**

**International application No.**

PCT/AU20 10/001 557

**A. CLASSIFICATION OF SUBJECT MATTER**

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<td><strong>C07D 15/08</strong> (2006.01)</td>
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<tr>
<td><strong>C07W 7/06</strong> (2006.01)</td>
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According to International Patent Classification (IPC) or to both national classification and IPC.

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

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

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

EPDOC, WPI, CAPLUS (Keywords -spodumene, lithium carbonate, ion exchange)

**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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<tbody>
<tr>
<td>Y</td>
<td>CA 1297265 C (METALLGESELLSCHAFT AKTDENGESELLSCHAFT) 17 March 1992 Abstract &amp; Figure 1</td>
<td>1-34</td>
</tr>
<tr>
<td>Y</td>
<td>GB 7708 12 A (BORAX CONSOLIDATED LIMITED) 27 March 1957 Example 1</td>
<td>1-34</td>
</tr>
<tr>
<td>Y</td>
<td>U.S. 6048507 A (AMOUZEGAR et al.) 11 April 2000 Column 4, lines 25-45 &amp; Figure 1</td>
<td>1-34</td>
</tr>
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</table>

**X** Further documents are listed in the continuation of Box C. **X** See patent family annex

* Special categories of cited documents:

A document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"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

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search: 13 December 2010

Date of mailing of the international search report: 20 DEC 2010

Name and mailing address of the ISA/AU:

AUSTRALIAN PATENT OFFICE
PO BOX 200, WODEN ACT 2606, AUSTRALIA
E-mail address: pct@ipaustralia.gov.au
Facsimile No. +61 2 6283 7999

Authorized officer:

MARYKA GAUDIO

AUSTRALIAN PATENT OFFICE

Telephone No: (02) 6225 6128

Form PCT/ISA/210 (second sheet) (July 2009)
## 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>
</tr>
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<tbody>
<tr>
<td>Y</td>
<td>US 6592832 B1 (FRIEDRICH et al.) 15 July 2003 Abstract and column 3, lines 1-8</td>
<td>1-34</td>
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<td>Y</td>
<td>US 2004/0005267 A1 (BORYTA et al.) 8 January 2004 Figure 4 &amp; paragraphs [0083]-[0088]</td>
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</table>
**INTERNATIONAL SEARCH REPORT**

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

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

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

2. [ ] Claims Nos.: 35  
   because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
   The claims do not comply with Rule 6.2(a) because they rely on references to the description and/or drawings.

3. [ ] Claims Nos.:  
   because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a)

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

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

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

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

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

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

**Remark on Protest**

[ ] The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

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

[ ] No protest accompanied the payment of additional search fees.
This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.

END OF ANNEX