such art forms a part of the common and/or general knowledge of a person of ordinary skill in the art. The above references are also not intended to limit the application of the process and system as disclosed herein.

SUMMARY OF THE DISCLOSURE

In an aspect, there is provided a process for producing a lithium product from a solution comprising lithium nitrate, the process comprising:

a. subjecting the solution comprising lithium nitrate to a first thermal treatment procedure in which water and nitric acid (when present) are removed, thereby forming a slurry comprising lithium nitrate crystals, and whereby the slurry comprising lithium nitrate crystals is heated to produce a molten liquid;

b. passing the molten liquid to a second thermal treatment procedure in which the molten liquid is heated to substantially decompose lithium nitrate to lithium oxide.

Disclosed herein in an example is a process for producing a lithium product from a solution comprising lithium nitrate. The solution comprising lithium nitrate may be obtained by reacting a lithium-containing metal silicate with nitric acid. For example, the solution comprising lithium nitrate may be obtained by the process disclosed in WO2017/106925. Herein, the term “lithium product” can include lithium nitrate, lithium oxide, lithium carbonate, lithium hydroxide, and lithium metal (amongst other products comprising lithium).

The process can comprise subjecting the solution comprising lithium nitrate to a first thermal treatment procedure. In the first thermal treatment procedure, water and nitric acid (when present) can be removed. The resultant lithium nitrate-rich crystal slurry can be heated to produce a molten liquid. The heating to produce the molten liquid may take place in a separate vessel/stage.

The process can also comprise passing the molten liquid to a second thermal treatment procedure. In the second thermal treatment procedure, the molten liquid may be heated to substantially decompose lithium nitrate to lithium oxide. As above, the lithium oxide may be the “lithium product” produced by the process, or the lithium oxide may be further processed to produce e.g. lithium carbonate, lithium hydroxide and/or lithium metal (amongst other products).

The process and system disclosed herein has distinct advantages over the prior art in that battery grade lithium hydroxide and marketable grade lithium carbonate may

be produced from a solution comprising lithium nitrate using a relatively simple flowsheet. For example, the process and system can have less purification steps than previous processes known in the prior art (including the applicant's process disclosed in WO2017/106925), decreasing the capital/operating costs and operational complexity.

In addition, the relative simplicity allows the process and system as disclosed herein to be installed adjacent to existing lithium mines and concentrators. For example, the process and system can be 'modularised/containerised', as explained in more detail below. A facility for the process and system can be owned and operated by the same owners/operators as the mines/concentrators, allowing them to value-add to their initial product. The flexibility of the process and system can further allow owners/operators to

terminate the process at e.g. a stage wherein lithium oxide is the final product. As lithium oxide contains a high percentage of lithium by weight, transportation of a lithium oxide product secures even greater reductions in freight costs than transporting the more familiar final lithium products (hydroxide/carbonate). The lithium oxide can be sold directly to e.g. battery plants, which can convert the less-pure oxide to high-purity lithium hydroxide as required, in their own facilities. Alternatively, the owner/operator may decide to process high-purity lithium hydroxide (and carbonate) on-site with the simple addition of further equipment (e.g. a lithium hydroxide crystalliser).

In some examples, in the second thermal treatment procedure, the lithium oxide produced during the decomposition of lithium nitrate may be allowed to float to the top of the molten liquid, thereby producing an overflow of lithium oxide and lithium nitrate slurry, and an underflow of lithium nitrate liquor. Such a flotation stage can facilitate separation of lithium nitrate from the lithium oxide.

In this regard, in some examples, the process may further comprise passing the lithium oxide and lithium nitrate slurry to a separation stage. In the separation stage, the lithium nitrate may be substantially removed from the lithium oxide. For example, the separation stage may produce lithium oxide crystals.

For example, in some examples, the separation stage may comprise a liquids removal stage in which the lithium nitrate is substantially removed as a liquid from the lithium oxide solids, thereby producing lithium oxide crystals. For example, the liquids removal stage may comprise a screw-press.

In some examples, the lithium oxide crystals may be passed to a slaking stage. In the slaking stage, a controlled amount of water may be added to the lithium oxide crystals and a solution comprising lithium hydroxide monohydrate may thereby be produced. The solution comprising lithium hydroxide monohydrate may constitute a product of the process.

In some examples, the solution comprising lithium hydroxide may be subjected to a crystallisation stage (e.g. to produce a purer form of lithium hydroxide monohydrate). In the crystallisation stage, the solution of lithium hydroxide may be concentrated and crystallised to form crystalline lithium hydroxide monohydrate.

In some examples, the crystallised lithium hydroxide monohydrate may be separated from solution, thereby producing a substantially liquid-free crystallised lithium hydroxide product. For example, the separation may be achieved by centrifugation. The resultant lithium hydroxide monohydrate crystals may constitute a

product of the process.

In some examples, the lithium nitrate liquor removed from the lithium oxide during the separation stage may be collected for further processing. For example, the further processing may comprise the addition of a carbonate compound to the lithium nitrate liquor (e.g. in a lithium carbonate precipitation stage) such that the lithium may react with carbonate, thereby producing lithium carbonate. The further processing may be performed under conditions that promote the precipitation of lithium carbonate.

In some examples, the lithium carbonate precipitate may be separated from solution. For example, the separation may be achieved by using a dewatering centrifuge. The lithium carbonate precipitate may constitute a product of the process.

In some examples, the solution separated from the lithium carbonate precipitate may be recycled as an alkali solution. The alkali solution may be used in a process stage of the reaction of the lithium-containing metal silicate with nitric acid. The alkali solution may be used as a neutralising solution.

In some examples, the carbonate compound may comprise sodium carbonate and/or potassium carbonate, such as can arise by adding sodium carbonate or potassium carbonate as the carbonate compound.

In some examples, the solution separated from the crystallised lithium hydroxide monohydrate may be passed to said carbonate compound further processing. For example, the separated solution may be passed to the lithium carbonate precipitation stage.

In some examples, the first thermal treatment procedure may comprise a two-stage thermal treatment. The two-stage thermal treatment may comprise a first heating stage in which the solution comprising lithium nitrate is heated to near-boiling to remove water and nitric acid (when present). The two-stage thermal treatment may further comprise a second heating stage in which a resultant near-boiling slurry of lithium nitrate is heated to a temperature of about 400 °C to melt the lithium nitrate in the slurry. Typically, because these stages operate at different temperatures, the stages (e.g. vessels) are separated. However, the stages may be performed in a single vessel operated under different conditions.

In some examples, the first thermal treatment procedure may produce a vapour stream comprising water and nitric acid (when present). The vapour stream may be collected and condensed. For example, the condensed vapour stream may provide process water and/or a dilute nitric acid solution.

In some examples, the temperature within the molten lithium nitrate in the second thermal treatment procedure may be about 600 °C. Such temperatures may cause molten lithium nitrate to decompose into lithium oxide and oxides of nitrogen. The gaseous stream which comprises oxides of nitrogen may be collected and e.g. passed to a nitric acid production process. The nitric acid can be recycled for extracting more lithium from a lithium silicate mineral feedstock to the process.

In some examples, the solution comprising lithium nitrate that is passed to the first thermal treatment procedure may be substantially free of contaminants. For example, the lithium nitrate solution may have been treated in accordance with the purification procedures as set out in WO2017/106925.

For example, the solution comprising lithium nitrate that is passed to the first thermal treatment procedure may be produced by an extraction process in which a lithium-containing metal silicate may be reacted with nitric acid. The extraction process may comprise mixing the silicate mineral with the nitric acid. The extraction process may also comprise subjecting the mixture to a leaching process having conditions such that the lithium values in the silicate mineral may be leached into an aqueous phase as lithium nitrate.

The extraction process may further comprise passing the leach solution through to a solids-liquids separation stage to remove remaining solids.

The extraction process may still further comprise optionally heating the separated leach liquor to distil off water and nitric acid as a vapour stream. The water and nitric acid vapour stream may be collected and used in the regeneration of nitric acid. The nitric acid can be recycled for extracting more lithium from the lithium silicate mineral feedstock.

The extraction process may additionally comprise subjecting the leach liquor to a series of reaction conditions such that contaminants may be substantially precipitated from the liquor. The extraction process may finally comprise passing the solution through a filtration stage to remove precipitates, thereby producing a substantially contaminant free solution comprising lithium nitrate which may then be passed to the first thermal treatment procedure.

In some examples, the nitric acid generated from the vapour stream of the second thermal treatment procedure may form at least a portion of the nitric acid mixed with the silicate mineral in the extraction process.

In some examples, the lithium-containing metal silicate may comprise spodumene ($LiAlSi_2O_6$). The lithium-containing metal silicate may also comprise any

of a range of other lithium-containing silicate minerals including but not limited to petalite $LiAlSi_4O_{10}$, eucryptite $LiAlSiO_4$, amblygonite $(Li,Na)AlPO_4(F,OH)$, and various minerals in the mica group including lepidolite $K(Li,Al,Rb)_3(Al,Si)_4O_{10}(F,OH)_2$ and zinnwaldite $KLiFeAl(AlSi_3)O_{10}(OH,F)_2$. The lithium-containing metal silicate may also comprise the lithium-boron mineral jadarite $LiNaSiB_3O_7(OH)$ or also written as $Na_2O.Li_2O.(SiO_2)_2.(B_2O_3)_3.H_2O$

In another aspect, there is provided a system that is configured to produce a lithium product from a solution comprising lithium nitrate, the system comprising:

a. one or more vessels that are configured such that the solution comprising lithium nitrate is able to be heated therein to an extent whereby water and nitric acid (when present) are removed as vapour and a resultant lithium nitrate-rich crystal slurry forms a molten liquid;

b. a further vessel that is configured to heat the molten liquid to substantially decompose lithium nitrate to lithium oxide.

Also disclosed herein, in another example, is a system for producing a lithium product from a solution comprising lithium nitrate. As above, the lithium product produced by the system can include lithium nitrate, lithium oxide, lithium carbonate, lithium hydroxide, and lithium metal (amongst other products comprising lithium). The system comprises one or more heated vessels in which the solution comprising lithium nitrate is able to be heated to an extent whereby water and nitric acid (when present) may be removed as vapour and a resultant lithium nitrate-rich crystal slurry may form a molten liquid.

The system may also comprise a further-heated vessel in which the molten liquid may be heated to substantially decompose lithium nitrate to lithium oxide.

In some examples, the further-heated vessel may be configured as a flotation cell. In the further-heated vessel thereby configured, as the lithium nitrate is decomposed, the lithium oxide may float, thereby producing an overflow of lithium oxide and lithium nitrate slurry, and an underflow of lithium nitrate. The overflow may be passed to a solids-liquid separation stage.

In some examples, the further-heated vessel may produce a gaseous stream comprising oxides of nitrogen. The further-heated vessel may also be sealed to prevent such gases from escaping into the atmosphere. In some examples, the further-heated vessel may be heated indirectly, such as by electrical induction.

In some examples, the solids-liquids separation stage may comprise a screw press in which the lithium oxide may be substantially separated from the lithium nitrate.

In some examples, the one or more heated vessels may comprise an evaporator. In the evaporator, the solution comprising lithium nitrate may be heated so as to cause evaporation of water as vapour along with nitric acid (when present) and an over-saturated solution of lithium nitrate may thereby be produced.

In some examples, the one or more heated vessels may further comprise a melting vessel to which the saturated to over-saturated solution of lithium nitrate may be passed. In the melting vessel, the over-saturated solution of lithium nitrate may be heated to melt the lithium nitrate. The melting vessel may be heated directly, or

indirectly, such as by electrical induction.

As above, the one or more heated vessels may comprise an evaporator that is separate to the melting vessel. However, in some examples, evaporation and melting may be performed in a single vessel that is operated under different conditions.

In some examples, the system may further comprise a nitric acid plant. The gaseous stream comprising oxides of nitrogen produced mainly by the further-heated vessel may be passed to the nitric acid plant to thereby produce nitric acid. As above, the nitric acid can be recycled for extracting more lithium from the lithium silicate mineral feedstock.

In some examples, a condenser may be arranged to collect and condense vapour from the one or more heated vessels and, when present, from the evaporator.

In some examples, the system may further comprise apparatus arranged to produce a crystalline lithium hydroxide product from the lithium oxide produced by the further-heated vessel.

In some examples, the system may further comprise apparatus arranged to produce a lithium carbonate product from the lithium nitrate-containing underflow. The apparatus may also be arranged to produce a lithium carbonate product from the lithium nitrate produced by the solids-liquid separation stage.

BRIEF DESCRIPTION OF THE DRAWINGS

Embodiments of a process and system will now be described, by way of example only, with reference to the following drawings in which:

Figure 1 is a generalised block flow diagram of the overall process for recovering lithium products from a lithium-containing silicate mineral.

Figure 2 is a schematic of a process flow diagram of a process by which lithium is recovered from a solution comprising lithium nitrate.

Figure 3 is a schematic of a process flow diagram of a first thermal treatment procedure.

Figure 4 is a schematic of a process flow diagram of a second thermal treatment procedure.

Figure 5 is a schematic of a process flow diagram of a nitric acid production facility.

Claims

1. A process for producing a lithium product from a solution comprising lithium nitrate, the process comprising:

a. subjecting the solution comprising lithium nitrate to a first thermal treatment procedure in which water and nitric acid (when present) are removed, thereby forming a slurry comprising lithium nitrate crystals, and whereby the slurry comprising lithium nitrate crystals is heated to produce a molten liquid;

b. passing the molten liquid to a second thermal treatment procedure in which the molten liquid is heated to substantially decompose lithium nitrate to lithium oxide.

2. A process as claimed in claim 1, wherein, in the second thermal treatment procedure, the lithium oxide produced during the decomposition of lithium nitrate is allowed to float to the top of the molten liquid, thereby producing an overflow of lithium oxide and lithium nitrate slurry, and an underflow of lithium nitrate liquor.

3. A process as claimed in claim 2, further comprising passing the overflow lithium oxide and lithium nitrate slurry to a separation stage in which lithium nitrate is substantially removed from the lithium oxide.

4. A process as claimed in claim 3, wherein the lithium oxide in the overflow of lithium oxide and lithium nitrate slurry comprises lithium oxide crystals, and wherein the separation stage comprises a liquids removal stage, in which the lithium nitrate is removed with liquid from the lithium oxide crystals.

5. A process as claimed in claim 3 or 4, further comprising:

adding water to the lithium oxide crystals, thereby producing a solution comprising lithium hydroxide monohydrate;

passing the solution comprising lithium hydroxide monohydrate to a crystallisation stage in which the solution of lithium hydroxide monohydrate is crystallised to form crystalline lithium hydroxide monohydrate.

6. A process as claimed in claim 5, further comprising separating the crystalline lithium hydroxide monohydrate from solution, thereby producing a substantially liquid free crystallised lithium hydroxide product.

7. A process as claimed in any one of claims 3 to 6, further comprising collecting the lithium nitrate removed from the lithium oxide during the separation stage for further processing, and wherein the further processing comprises:

adding a carbonate compound to the lithium nitrate such that lithium reacts with carbonate thereby producing lithium carbonate;

subjecting the lithium carbonate to conditions under which the lithium carbonate precipitates, thereby producing a lithium carbonate precipitate; and

separating the lithium carbonate precipitate from solution.

8. A process as claimed in any one of the preceding claims, wherein the first thermal treatment procedure comprises a two-stage thermal treatment comprising:

i. a first heating stage in which the solution comprising lithium nitrate is heated to a temperature at which water and nitric acid (when present) are removed therefrom, thereby forming the slurry comprising lithium nitrate crystals;

ii. a second heating stage in which the slurry comprising lithium nitrate crystals is heated to a temperature of about 400 °C to melt the lithium nitrate in the slurry, thereby forming the molten liquid.

9. A process as claimed in any one of the preceding claims, wherein the first thermal treatment procedure produces a vapour stream comprising water and nitric acid (when present), and wherein said vapour stream is collected and condensed.

10. A process as claimed in any one of the preceding claims, wherein the second thermal treatment procedure is performed at a temperature of about 600 °C.

11. A process as claimed in any one of the preceding claims, wherein the second thermal treatment procedure produces a gaseous stream comprising oxides of nitrogen, and wherein said oxides of nitrogen are passed to a nitric acid production process.

12. A process as claimed in any one of the preceding claims, further comprising, prior to step a., reacting a lithium-containing metal silicate with nitric acid to obtain the solution comprising lithium nitrate.

13. A process as claimed in claim 12, wherein the solution comprising lithium nitrate is a substantially contaminant free solution comprising lithium nitrate, and wherein the process comprises:

i) mixing the lithium-containing metal silicate with the nitric acid to obtain a mixture;

ii) subjecting the mixture to a leaching process having conditions such that the lithium values in the lithium-containing metal silicate are leached into an aqueous phase as lithium nitrate, thereby forming a leach solution;

iii) passing the leach solution through to a solids-liquids separation stage to remove solids and obtain a leach liquor;

iv) subjecting the leach liquor to reaction conditions such that contaminants are substantially precipitated, thereby producing a leach liquor with precipitates;

v) passing the leach liquor with precipitates through a filtration stage to remove the precipitates, thereby producing the substantially contaminant free solution comprising lithium nitrate for passing to the first thermal treatment procedure.

14. The process according to claim 13, the process further comprising, prior to step iv), heating the leach liquor to distil off water and nitric acid as a gas stream, with the water and nitric acid gas stream collected and used in the regeneration of nitric acid.

15. A process as claimed in any one of the preceding claims, wherein the lithium-containing metal silicate is one or more of: spodumene $LiAlSi_2O_6$, petalite $LiAlSi_4O_{10}$, eucryptite $LiAlSiO_4$, amblygonite $(Li,Na)AlPO_4(F,OH)$, lepidolite $K(Li,Al,Rb)_3(Al,Si)_4O_{10}(F,OH)_2$ and zinnwaldite $KLiFeAl(AlSi_3)O_{10}(OH,F)_2$.

16. A system that is configured to produce a lithium product from a solution comprising lithium nitrate, the system comprising:

a. one or more vessels that are configured such that the solution comprising lithium nitrate is able to be heated therein to an extent whereby water and nitric acid (when present) are removed as vapour and a resultant lithium nitrate-rich crystal slurry forms a molten liquid;

b. a further vessel that is configured to heat the molten liquid to substantially decompose lithium nitrate to lithium oxide.

17. A system as claimed in claim 16, wherein the further vessel is configured as a flotation cell in which, as the lithium nitrate is decomposed, the lithium oxide floats, thereby producing an overflow of lithium oxide and lithium nitrate slurry, and an underflow of lithium nitrate.

18. A system as claimed in claim 17, further comprising a solids-liquid separation stage configured to receive the overflow of lithium oxide and lithium nitrate slurry, wherein the

solids-liquid separation stage comprises a screw press capable of substantially separating the lithium oxide from the lithium nitrate.

19. A system as claimed in any one of claims 16 to 18, wherein the one or more vessels comprises an evaporator configured to heat the solution comprising lithium nitrate so as to cause evaporation of water and evaporation of nitric acid (when present) and thereby produce an over-saturated solution of lithium nitrate.

20. A system as claimed in claim 19, wherein the one or more vessels further comprises a melting vessel configured to receive the over-saturated solution of lithium nitrate and which is capable of heating the over-saturated solution of lithium nitrate to melt the lithium nitrate.

21. A system as claimed in any one of claims 16 to 20, wherein the further vessel is configured to produce a gaseous stream comprising oxides of nitrogen, with the further vessel being sealed to prevent such gases from escaping into the atmosphere, and wherein the system further comprises a nitric acid plant configured to receive the gaseous stream comprising oxides of nitrogen produced by the further vessel and to produce nitric acid therefrom.

22. A system as claimed in any one of claims 16 to 21, further comprising a condenser that is arranged to collect and condense vapour from the one or more vessels and, when present, from the evaporator.

23. A system as claimed in any one of claims 16 to 22, further comprising an apparatus configured to produce a crystalline lithium hydroxide product from the lithium oxide produced by the further vessel.

24. A system as claimed in claim 17 or 18, or any one of claims 19 to 23 when dependent on claims 17 or 18, further comprising an apparatus configured to produce a lithium carbonate product from the lithium nitrate underflow and from the lithium nitrate produced by the solids-liquid separation stage.

25. A process as claimed in any one of claims 1 to 3, further comprising reducing the lithium oxide to form lithium metal.

26. A process as claimed in any one of claims 1 to 15, wherein the solution comprising lithium nitrate is prepared by a process comprising:

i) mixing a lithium-containing metal silicate with nitric acid to form a mixture;

ii) subjecting the mixture to a leaching process wherein lithium values in the lithium-containing metal silicate are leached from the lithium-containing metal silicate as lithium nitrate, thereby forming the solution comprising lithium nitrate.

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