Abstract:

Method and apparatus for producing beta-spodumene from material containing alpha-spodumene granules. According to the method, the alpha-spodumene concentrate is heated to a temperature of more than 800 °C in order to convert the alpha-spodumene into beta-spodumene. According to the invention, heat is brought to the heating zone by indirect heating, when at least some of the heat is brought with the aid of heat-transfer pieces, which are able to direct a grinding effect on the spodumene granules. In the heating zone, the temperature of the material containing alpha-spodumene granules is kept below the agglomeration temperature of the material containing, among other things, host rock, quartz, and spar as deads. After heating, the beta-spodumene can, if necessary, be enriched by screening it out of the other materials.
Method for Producing Beta-Spodumene from a Raw Material Containing Alpha-Spodumene

Field of the Invention

The present invention relates to a method, according to the preamble to Claim 1, for producing beta-spodumene from a raw material containing alpha-spodumene, particularly from a material containing alpha-spodumene granules, particularly from a concentrate.

In such a method, the material containing alpha-spodumene granules is heated at a temperature of at least 800 °C in order to convert the alpha-spodumene into beta-spodumene.

The invention also relates to an apparatus according to the preamble to Claim 29.

Background

An increasing amount of lithium salts, such as lithium carbonate and lithium ferrophosphate are used today in the manufacture of batteries. Lithium is obtained from natural salt solutions containing lithium and from various rock materials, such as spodumene, petalite, and lepidolite. The lithium is recovered and is exploited in various applications in the form of its salt. There are few uses for metallic lithium.

Spodumene, i.e. lithium aluminium silicate, LiAlSi₂O₆ (Li₂O·Al₂O₃·4SiO₂), is particularly interesting as a raw material, because its content in ore concentrate is relatively high and the lithium can be easily separated from it, for example, by pressure extraction performed using sodium carbonate, or by using a concentrated mineral acid, such as sulphuric acid. For example, after cleaning by using an ion-exchanger, an extremely pure product is recovered, mainly pure lithium carbonate.

Spodumene occurs in nature as alpha-spodumene, which, before the separation of the lithium, must be converted to beta-spodumene, in order to improve solubility. The change in the crystalline form is achieved by heat treatment. Thus, the manufacturing process of lithium carbonate generally includes a stage, in which the spodumene concentrate is heated
at a temperature of at least 800 °C, typically 800-1 100 °C. The beta-spodumene thus obtained is suspended in water to form a slurry, after which the desired lithium compound, such as lithium carbonate, can be produced, for example, by pressure extraction using sodium carbonate.

The patent literature describes methods for implementing the heat treatment intended to change the crystalline form. CA Application Publication No. 1 297 265 discloses a solution, in which 1-10-mm granules are treated in a circulating-mass reactor. The amount of circulating gas required in the method is relatively large and oxygen must be added separately at many points. As a result, the energy consumption of the process, and correspondingly the fuel consumption used to produce the heat is great, which increases environmental detriments, for instance, through emissions.

In turn, a method for producing beta-spodumene from alpha-spodumene with the aid of heat treatment is known from US Patent Application Publication US 2013/0042438, when the raw material used is a concentrate or ore of a smaller particle size than in the solution described above, the particle size being 20-1000 μm. Such small granules are treated in a fluidized bed at a temperature of 800-1000 °C. Oxidizing gases are used for the fluidization.

The known solution requires feed with a narrow granule-size distribution to be fed into the reactor, so that the solids can be fluidized as evenly as possible. The solution cannot be applied in cases, in which among the concentrate is material, for example, of a coarse granule size, along with the fine-grained source material obtained by flotation.

The prior art is further represented by the following reference publications: CA 630 368, US 2,994,523, CN 102494535, US 2,592,783, US 3,350,280, CN 201407891, and JP H01 167580.

Generally, the problem with the heat treatment of the prior art is the fact that the deads associated with spodumene, such as quartz and spar, as well as host rock, can easily agglomerate in connection with heat treatment that is excessively prolonged or performed at too high a temperature, which will make the extraction of the lithium difficult. On the other hand, heat treatment that is too short or performed at too low a temperature may, for
its part, can leave a significant part of the spodumene in the form of alpha-spodumene, which will reduce the average production yield.

Summary of the Invention

The present invention is intended to remove at least some of the drawbacks related to the prior art and create a new type of solution for producing beta-spodumene from a raw material containing alpha-spodumene with the aid of heat treatment.

The invention is based on the idea that the alpha-spodumene is fed into a heating zone, to which the heat required to change the crystal form is brought by indirect heating.

At least part of the heat is then brought most suitably with the aid of such transfer pieces, i.e. heat-transfer pieces, which are able to impose a grinding effect on the spodumene material.

In the heating zone, the temperature of the concentrate is kept under the agglomeration temperature of the spodumene material. The setting of this temperature is influenced not only by the spodumene material contained in the raw material, e.g., the spodumene granules it contains, but also by the host rock and deads, such as quartz and spar.

In the implementation of the invention an apparatus can be used, which comprises a rotary drum kiln, in which the raw material containing alpha-spodumene material can be heated at a temperature of more than 800 °C in order to convert the alpha-spodumene into beta-spodumene. In the drum kiln there is a kiln chamber delimited by a jacket, to which is connected and into which opens a transfer-piece feed pipe for feeding hot heat-transfer pieces in among the alpha-spodumene material to be heated in the kiln. The opposite end of the pieces' feed pipe is connected to a heating oven, in which the temperature of the pieces can be raised before they are fed into the drum kiln. An outlet pipe is further arranged to the drum kiln, with the aid of which the heated spodumene material can be removed from the drum kiln. The material obtained from the outlet pipe can preferably be directed to a screen, in which the pieces used to bring heat can be separated out.
More specifically, the method according to the invention is principally characterized by what is stated in the characterizing portion of Claim 1.

The apparatus according to the invention, is, for its part, characterized by what is stated in the characterizing portion of Claim 29.

Considerable advantages are gained by means of the solution according to the invention. When heat is brought indirectly, alpha-spodumene can be converted to the beta-form, e.g., at 950-1080 °C with a short delay time. By keeping the temperature in the range in question, conversion can be achieved without agglomeration taking place, particularly without the host rock and deads agglomerating.

By using for heat transfer solid pieces that store and release heat, and which are sufficiently hard to impose a mechanical effect, such as a grinding effect, on the raw material, it is possible to reduce the adhesion of the putty-like spodumene material to the metal surfaces of the kiln. Thus by using heat-transferring pieces, the adhesion of the spodumene to the inner walls of the drum kiln used for heating is reduced significantly or even substantially.

By using heat-transfer pieces, the average size of which is greater than that of the spodumene, the heat-bringing pieces can be separated after heating by screening, when host rock and quartz and other deads can also be screened out of the spodumene. This is based on the fact that, unlike the host rock particles and deads, such as quartz and spar, the spodumene itself becomes finer during heat treatment.

In the present solution, it is possible to treat flotation concentrate, sink-and-float concentrate, as well as mixtures of these, for which reason the granules and granule-size distribution of the concentrate or ore can vary over a wide range, which is not possible in the aforementioned known solutions.

For the reasons described above, the process is efficient and energy-economical; the converted spodumene can easily be removed from the heating zone and, because the host rock and deads have not agglomerated, they can be separated from the material removed from the heating zone, for example, cost-effectively by screening, as stated above.
In the following, the method and apparatus are examined with the aid of a detailed description, with reference to the accompanying drawings.

Brief Description of the Drawings

Figure 1 shows a simplified process diagram of one exemplary embodiment, Figure 2 shows a cross-sectional side view of the construction of a kiln according to an alternative embodiment, and Figure 3 shows a front view of the radiation plate.

Embodiments

As will be apparent from the above description, the present technology relates to the production of lithium carbonate in general. The raw material is, spodumene, a rock material with a lithium content. In terms of the production of lithium compounds, spodumene is very advantageous, as its lithium content is relatively great and the lithium can be quite easily extracted from it. The technology relates particularly to the heat-treatment stage of such a process, in which the material containing spodumene concentrate is heated in order to achieve a phase transformation.

The lithium carbonate production process begins with mechanical pre-treatment. The mined ore is pre-crushed in the mine area and the host rock is removed from the crushed material, for example, by magnetic separation or optical sorting. After this, the crushed material is pulverized, usually by grinding or crushing. Grinding can be performed using a mill, such as a rod or ball mill, and crushing by using a cone or roll crusher. Of course, other devices and apparatuses intended for the grinding and crushing of hard material can also be used.

The spodumene is most suitably separated from the ground ore by flotation. Flotation can be done using traditional flotation in the water stage. It is also possible to perform separation and enrichment using sink-and-float enrichment. The granule size of the concentrate then obtained (average granule size) is mainly in the range 0.1-20 mm, particularly about 0.6-6 mm.
The expressions used in the present connection "material containing alpha-spodumene granules", "(alpha-)spodumene material", as well as "alpha-spodumene raw material" cover alpha-spodumene concentrate, for example, in addition to the concentrate obtained in the manner described, also

- rough concentrate and
- ore or crushed ore made from it.

Thus, in one embodiment the raw material of the process is alpha-spodumene concentrate.

In a second embodiment, the raw material is rough concentrate. Rough concentrate is the fraction, which is obtained from the ore by pre-enrichment, for example, using sink-and-float enrichment. A significant part, for example about 30-50 % of the feed mass obtained by pre-crushing and possibly grinding, can typically be removed as waste. The rough concentrate can be heat treated as such in the manner described herein, after which the beta-spodumene is recovered from the material obtained, e.g., by screen enrichment.

In a third embodiment, the raw material is ore. The pre-crushed and possibly ground ore can be heat treated as such in the manner described herein, after which the beta-spodumene is recovered from the material obtained, e.g., by screen enrichment.

"Screen enrichment" refers to the separation and recovery of the desired granules by using one or several screens.

After mechanical pre-treatment, moisture is removed from the alpha-spodumene material most suitably at 150-400 °C. A kiln, (preheating kiln) can be used for moisture removal. The kiln can be heated for example, by an electrical resistance, bio-gas, combustion gas, liquid gas, or the cooling gas of the converted concentrate, or by a combination of the aforementioned heat-releasing gases. Of course, of course ordinary, e.g., solid or liquid fuels, can also be used to heat the kiln intended for moisture removal.

In the present invention, the term "electrical resistance" refers generally to heating resistances that can be connected to an electricity supply.
The spodumene material is heat treated, so that the crystalline structure is changed from the insoluble $\alpha$-form to the soluble $\beta$-form. Typically the material containing alpha-spodumene granules is heated in a heating zone at a temperature of over 800 °C, particularly at a temperature of over 950 °C, in order to achieve the phase transformation of the alpha-spodumene.

The alpha-spodumene of the available material contains, in its crystal lattices, at least some iron as an impurity. Typically, the amount of iron is about 0.01-1.3 % as a ferroxide, of the weight of the material being treated. The main deads types in the raw material are quartz $(\text{SiO}_2)$ and alkali spar, i.e. albite (NaAlSi$_3$O$_8$) and potassium feldspar (KAlSi$_3$O$_8$). The raw material can also contain host-rock particles from outside the ore, i.e. from the host rock.

In the heating zone, the temperature of the spodumene material and the spodumene granules it contains is held under the agglomeration temperature of these components that are also contained in the concentrate. Thus, the alpha-spodumene is most suitably brought to phase transformation at a temperature of 950-1080 °C, preferably 950-1050 °C.

In one embodiment, the heating zone comprises one first zone, in which the temperature of the alpha-spodumene granules is raised to at least 800 °C but less than the temperature required for the phase transformation of the alpha-spodumene, and a second zone, in which the temperature is raised to the temperature required for the phase transformation of the alpha-spodumene.

In the first embodiment, heating devices arranged in several series are used for the heating. For example, a kiln arranged in at least two series can be used, such as a drum kiln, in which case the alpha-spodumene granule fraction is first fed into a first kiln forming the first zone, in which the temperature of the alpha-spodumene granules is raised to at least 800 °C, when the material removed from this kiln is led to a second kiln forming the second zone, in which the temperature is raised to at least 950 °C.

The second kiln can, for its part, be divided into two heating zones, when the temperature of the alpha-spodumene granule fraction is raised in stages to at least 950 °C.
The aforementioned kilns are most suitably drum kilns, which are suitable for continuous operation. In these drum kilns there is typically a kiln chamber surrounded by a jacket.

Typically in the present technology, the drum kiln used as, for example, a pre-heating, conversion, and correspondingly cooling zone, comprises a rotatable cylinder, i.e. drum, the length of which can be 1-30 metres and the internal diameter (i.e. the diameter of the actual kiln chamber) about 0.1-5 m. The material to be treated is fed into the input end of the drum and the treated material is removed from the opposite end of the drum, i.e. its outlet end.

The drum is most suitably set to a slanting attitude, so that, looking from the input end of the drum, the central axis of the drum forms an acute angle relative to the horizontal plane, for example the angle can be about 0.1-20 degrees, for example, 0.5-15 or even 5-15 degrees relative to the horizontal plane. The delay time in the kiln can be about 1-180 minutes and the rotational velocity of the drum around the central axis is about 1-50 revolutions a minute.

The length of the drum, the angle attitude of the central axis, and the length and rotational velocity of the drum are selected according to the material being treated and its amount.

In one embodiment, thermal energy is brought to the conversion zone with the aid of heat-storing and releasing pieces. Most suitably the pieces are of a hard material, such as metal, ceramic material, or a mineral. The pieces can have a regular geometrical shape. They can be cylindrical, cubical, or spherical. Most suitably they are solid. One embodiment uses metal or ceramic balls that can be heated.

The heat-transfer pieces can also be three-dimensional pieces with an irregular and undefined external shape. In size, they are generally larger than the average granule size of the input to the process, so that they can be separate mechanically, for example by screening from the material removed from the conversion zone. Typically, at least 90 %, especially at least 95 %, and most suitably at least 99 % of the transfer pieces, are 6 mm or larger in size, most suitably at least 90 %, especially at least 95 %, most suitably at least 99 % of the transfer pieces are 20 mm or larger in size.
Most suitably, a separate oven is used to heat the heat-transfer pieces. This can be electrically heated. In one embodiment, an oven external to the conversion kiln is used. In a second embodiment, the heating oven is fitted inside the conversion kiln. The particular advantage of this solution is, among other things, that it is energy-efficient, because the waste heat from the oven is transferred to the conversion kiln. In addition, when implemented as a tubular structure, its outer surface forms a heat-transfer surface, from which heat can transfer by conduction to the material being treated.

The heating stage will be examined in yet greater detail with the aid of the accompanying drawings.

After the heating zone, further enrichment of the beta-spodumene can be performed by screening. In a preferred embodiment, the material removed from the heating zone is screened in order to separate host rock and deads, such as quartz and spar, from the beta-spodumene.

Lithium is recovered from the beta-spodumene obtained, in an as such known manner. In one embodiment, lithium is dissolved using a continuously operating sodium carbonate pressure-dissolution process. Dissolution can be performed, for example, in a water solution of sodium carbonate (Na$_2$C$_0$$_3$) at a temperature of 180-250 °C, particularly 200-220 °C, and a pressure of 10-30 bar, particularly about 20 bar.

In pressure dissolution, an ion-exchange reaction takes place, in which the sodium ions replace the lithium ions in the crystal lattice of the spodumene, forming a synthetic silicate, analcime (NaAlSi$_3$O$_8$-H$_2$O). For its part, the lithium moves to the water solution, when insoluble lithium carbonate (Li$_2$C$_0$$_3$) is formed.

The products of the pressure dissolution are recovered and are cooled at a selected temperature, generally the ambient temperature, most suitably about 20-25 °C. Carbon dioxide is added to the suspension at a pressure of 5-20 bar, particularly about 8-11 bar, in order to form soluble lithium hydro-carbonate (LiHCO$_3$) in the liquid phase. The solid analcime is first filtered out of the solution obtained, after which the LiHCO$_3$ solution is crystallized, when solid lithium carbonate is obtained.
The end product is exceptionally pure lithium carbonate, with a purity of more than 99.0 
%, preferably at least 99.5 %, most suitably more than 99.9 %, and even at least 99.99 %.

Methods for recovering lithium carbonate and purifying lithium bicarbonate are disclosed, 
for example, in application publications WO 2010/103173 and WO 2013/140039.

The following refers to the drawing according to Figure 1, which shows one exemplary 
apparatus solution, which is suitable for performing the phase-transformation of alpha-
spodumene.

According to the drawing, the apparatus comprises three heat-transfer zones connected in 
series, i.e. a pre-heating drum 1, a conversion drum 2, and a cooling drum 3.

In the solution of Figure 1, the heat required in the process is produced using a combustion 
boiler 8, in which organic material, such as a bio-fuel, is burned. In turn, the pressurized 
steam required in electricity production 10 is produced in a steam boiler 9. In the oxygen 
plant 7, in turn, oxygen is separated from the air. It should be emphasized that, in place of 
these apparatuses, other solutions can be used to produce the necessary heat.

The drums 1-3 can typically be rotated around their central axes and set at a suitable angle 
attitude, so that the material being treated travels through them by gravity. The drums can 
have similar dimensions.

The length of the conversion drum can be 2-25 m, particularly about 3-20 m, for example 
4-15 m. The diameter of its kiln chamber is, for example 0.1-5 m, such as 0.5-3 m.

In one embodiment, the pre-heating drum is shorter than the conversion drum, e.g., its 
length is 0.1 - 0.9-times the length of the conversion drum. In one embodiment the 
diameter of the pre-heating drum is greater than that of the conversion drum, e.g., its 
diameter is 1.1-3-times the diameter of the conversion drum.

In one embodiment, the cooling drum is at least slightly shorter than the conversion drum, 
e.g., its length is 0.1 - 0.9-times that of the conversion drum. In one embodiment, the
diameter of the cooling drum is greater than that of the conversion drum, e.g., its diameter is 1.1-3-times that of the conversion drum.

In the pre-heating drum marked with the reference number 1, moisture is removed from the alpha-spodumene material at a temperature of about 150-400 °C. Hot combustion gas available from the following stage, i.e. the conversion drum 2, is used for heating, as shown in the figure. As stated above, electricity or a separate burner can be used for heating.

From the pre-heating drum, the material is fed to the jacketed 2' conversion drum 2, which forms the heating zone for performing the phase transformation of the alpha-spodumene. In the drum kiln, the material containing alpha-spodumene is heated to a temperature of 800 °C, preferably of at least 950 °C.

The drum is divided into two part, so that the first part of the drum - in the direction of travel of the concentrate - is heated indirectly by combustion gases, whereas the latter part, which forms the actual conversion zone, is heated by indirect heating. Part of the heat is produced by electric heating 12, particularly by electrical resistances, and part of the heat with the aid of heat-storing and releasing pieces 13. Thus, heat is brought to the drum kiln by conduction through its jacket and, in addition, by radiation. Of course it is possible to also implement the heating of the first part at least partly by electric heating.

In the drum kiln there is a kiln chamber 2' equipped with an alpha-spodumene granule feed connection 14 and surrounded by a jacket 2" and in which there is further a beta-spodumene removal connection 15.

In the jacket 2" of the kiln is a gas input connection 16 used for heating and a heat releasing gas outlet connection 17 for bringing heat through the jacket of the drum kiln. In the heating zone 2, the temperature of the concentrate is kept at least that the agglomeration temperature of the side-components contained in the concentrate, such as host rock and deads. The spodumene concentrate typically contains quartz and spar as deads and similar substances and rock materials containing silica, which may agglomerate due to the effect of the heating.
In the first part of the drum kiln, the temperature is raised to close to, but not quite the temperature needed for the phase transformation of alpha-spodumene. Thus, in the first part, the temperature is usually more than 800 °C but less than 950 °C, and in the second it is raised to the temperature required for phase transformation, i.e. to at least 950 °C.

An alpha-spodumene fraction, the average size of the granules of which is 0.5-6 mm, is fed to the heating zone 2.

As has been stated above, in the invention a feed with a wide granule-size distribution can be treated. Thus, in one embodiment, a first alpha-spodumene granule fraction, the average granule size of which is 0.5-6 mm, and a second alpha-spodumene granule fraction, the average granule size of which is 0.02-1 mm, are fed to the heating zone, the first and second granule fractions being fed to the heating zone either simultaneously or consecutively.

The heat-bringing pieces 13 are heated in a heating oven 11 for the pieces, which is heated using combustion gas which, in the case according to the drawing is obtained from a combustion boiler 8, in which a bio-fuel, for example, is burned. In the drum kiln, there is a feed connection 18 for the hot pieces, which opens into the kiln chamber delimited by the jacket, for feeding the transfer pieces in amount the alpha-spodumene granules to be heated in the kiln, when the intermediate-piece feed connection is connected to the oven 11, in which the temperature of the pieces can be raised. Figure 1 shows two alternative feeding points for the pieces.

The heat-transfer pieces release heat to the material to be heated. Most suitably the heat-bringing pieces 13 are of metal, ceramic material, or a rock material, preferably the transfer pieces have a cylindrical, cubical, spherical, or irregular three-dimensional shape. In order to create a mechanical effect on the spodumene, the pieces have a hard surface. The pieces mix with the material being treated and impose a grinding effect on the spodumene granules as the drum rotates. At the same time, the pieces scrape the putty-like spodumene from the surface of the drum and prevent the spodumene from creating a layer on the inner surface of the drum.
The beta-spodumene is recovered as the product (removed material) of the heating zone through the removal connection 15. This is connected to a screen 4, with the aid of which the transfer pieces used to bring heat can be separated from the removed material.

In one embodiment, the screen 4 is used to separate out the pieces and allows the rest of the material through. The mesh size of the screen 4 can therefore be chosen according to the size of both the feed and the pieces.

In one embodiment, a mesh size is chosen, which is at most 20.0 mm and particularly 6.0 mm or greater than that, when the transfer pieces will be effectively separated.

The aforementioned has the advantage that, when feeding material, which has an average granule or particle size of 0.5-6.0 mm, to the process, all the crushed ore can pass the screen 4, so that it is possible to prevent, for example, pieces of ore, host rock, or deads from travelling with the transfer pieces, when they might agglomerate, or melt with the transfer pieces in the heating oven 11.

The pieces separated from the material removed from the heating zone are led without cooling to the heating 11, to raise their temperature to the preselected temperature, after which they are recirculated for re-use in the heating zone.

On the basis of the above, in one embodiment the product removed from the heating zone is first screened using a screen 4, the mesh size of which is 6.0 mm or greater, so that the heat-bringing pieces are separated. The part passing the screen being screened by a second screen 5 after optional cooling.

In one embodiment, beta-spodumene is produced, which comprises granules that pass a screen, the mesh size of which is at least 0.3 mm, and at most about 1.2 mm, most suitably about 0.5-1 mm, e.g., about 0.7 mm.

The mesh size of the second screen 5 is most suitably about 0.3-1.0 mm (e.g. about 0.7 mm), when the beta-spodumene is recovered as the part passing the latter screen.
The beta-spodumene obtained is cooled before or after the second screen to a temperature of about 100-250 °C, at which it is recovered. Reference number 6 shows a thermo-silo, which is intended for storing the recovered spodumene at the desired temperature. The cooling drum 3 can be according to the drawing, when, in the first stage, the product, which has travelled through the heating zone 2 and first screen 4 is cooled first by gas and then by water cooling. The gas is obtained, for example, from the oxygen plant 7, where the nitrogen and oxygen of the air are separated from each other, so that the nitrogen can be used as the medium of the gas cooling of the cooling drum. For its part, the oxygen is used for the combustion of the bio-fuel in the combustion unit 8.

The beta-spodumene obtained from the cooling is screened by the second screen 5, as described above.

The beta-spodumene thus obtained, typically at 100-250 °C, is taken to solution treatment, where the lithium it contains is separated by dissolving.

As stated above, the heating zone can be in two parts or can consist of two heating zones connected in series.

In one preferred embodiment, the drum kiln 2 shown in Figure 1 is divided in the middle by a radiation plate, which thermally separates the two zones from each other, in which there are different temperatures. The heat-storing and releasing transfer pieces can be fed behind the radiation plates (in the direction of travel of the spodumene). Figure 3 shows an example of the configuration of the radiation plate. As the figure shows, an opening can be formed in the plate, which is, e.g., segment-shaped, and through which the material being treated is moved. The opening preferably extends to the edge of the plate. The size of the opening is most suitably about 5 - 50 % of the surface area of the entire plate. The plate is preferably permanently fixed in place, so that it rotates along with the kiln.

Figure 2 shows an alternative implementation of the heating kiln.

The embodiment according to Figure 2 comprises a conversion kiln 20, in which there is a pre-heating zone 21 and a conversion zone 22, which are arranged consecutively and in the said order in the direction of the progression of the material (broken-line arrow 37). The
pre-heating zone is equipped with a feed connection 29 for the material to be treated and the conversion zone correspondingly with a removal connection 30 for the treated material. The conversion kiln according to the figure is a drum kiln, which comprises a cylindrical jacket 23, which is surrounded by thermal insulation 24 arranged outside the jacket. In the jacket are heating resistances 25 to bring heating energy to the kiln. The kiln is rotatable.

The feed and correspondingly removal ends of the conversion kiln 20 are closed with radiation plates 26 (see Figure 3) and 28 to reduce heating-energy loss. In addition, inside the conversion kiln 20, roughly in its centre, is arranged a radiation plate 27, which thermally separates from each other the conversion kiln's pre-heating zone 21, in which the material obtained from the pre-heating unit is raised to close to the phase-transformation temperature of alpha-spodumene, and correspondingly a conversion zone 22, in which the temperature is raised above the phase-transformation temperature of alpha-spodumene.

In the conversion zone, a heating oven 31 is further arranged which comprises two concentric pipes 32, 33, in the annular space between which heating resistances 34 are arranged to heat the oven. In the following, the heating oven 31 is referred to as the "pipe oven". Inside it, the heat-transfer pieces 35 can be heated, which are referred to in the following as "auxiliary heating balls".

The resistances 34 of the heating oven 31 for the auxiliary heating balls 35 direct heat both by conduction and radiation inwards from the innermost oven pipe 32, when it heats the balls 35, and outwards from the outermost pipe 33, when it heats the material to be treated.

The front end of the pipe oven (in the direction of travel of the material being treated) is attached to a radiation plate 27. Most suitably, the attachment point of the pipe oven 31 and the radiation plate 27 is located at a point deviating from intersection of the central axis of the drum kiln and the plane of the radiation plate, i.e. the attachment is eccentrically implemented, so that the height position of the front end of the pipe oven changes according to the rotational movement of the conversion kiln. The auxiliary heating balls can then drop by gravity to the conversion zone 22 of the kiln, when the oven pipe is in the lower position, i.e. its central axis is at a lower level than the central axis of the drum kiln. Between the pipe oven 31 and the inner chamber of the conversion kiln a not-shown
connection is formed, which attenuates the transfer movement of the auxiliary heating balls from the heating oven 31 to the conversion zone 22.

As space appears in the heating oven 31, auxiliary heating balls 35 are fed into it from the connection 36. A screen-like opening (not shown) is then formed in the pipe body 32, 33 of the heating oven, most suitably on the opposite side to the connection 36, from which spodumene that has come along with the balls is returned to the conversion zone 22 of the conversion kiln 20.

The balls 35 obtained from the heating oven heat and grind the material to be treated in the conversion zone on the bottom of the kiln 22, which helps avoid the material from becoming like putty, or even prevents this entirely. Unlike the host-rock particles and deads, the spodumene becomes finer by itself during the heat treatment.

Protrusion or bumps (not shown) can be formed on the inner surface of the conversion kiln's 20 jacket, which mix and lift the material being treated when the drum rotates. The concentrate rising along with these lifters then drops on top of the outer pipe 33. The heat is then directed effectively also from the surface of the outer pipe to the material being treated.

As described in connection with the previous embodiment, if necessary, a screen can be arranged after this kiln too to separate the beta-spodumene and host-rock particles and deads from each other.

The pipes forming the conversion kiln 20 and heating oven 31 are of a fire-resistant material, particularly fire-resistant steel or a fire-resistant metal alloy, for example, a nickel and chrome-rich alloy.

**Industrial applicability**

The present solution is suitable for the production of beta-spodumene. Lithium compounds suitable, for example, for battery applications, can, in turn, be manufactured from beta-spodumene.
Reference Numerals List

1. Pre-heating drum
2. Conversion drum
5  2' Jacket
   2" Kiln chamber
3. Cooling drum
4. Screen 6.0 mm
5. Screen 0.7 mm
10  6. Thermo-silo
7. oxygen plant
8. Bio-combustion
9. Steam boiler
10. Electricity production
15 11. Transfer pieces heating
12. Electrical resistances
13. Heat-transfer pieces
14. Feed connection for alpha-spodumene material
15. Removal connection for beta-spodumene
20 16. Gas inlet connection
17. Gas outlet connection
18. Heat-transfer pieces feed points
20. Conversion kiln
21. Pre-heating zone
25 22. Conversion zone
23. Jacket
24. Insulation
25. Electrical resistances
26., 27., 28. Radiation (protection) plate
30 29. Feed connection
30. Removal connection
31. Heating oven
32., 33. Pipes
34. Electrical resistances
35 35. Auxiliary heating balls
36. Auxiliary heating balls feed connection
37. Direction of movement of material being treated
38. Direction of movement of heating pieces
40

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Claims:

1. Method for producing beta-spodumene from material containing alpha-spodumene granules, according to which method

5. the material containing alpha-spodumene granules is heated in a heating zone at a temperature of more than 800 °C in order to convert the alpha-spodumene into beta-spodumene, characterized in that

- heat is brought to the heating zone at least mainly by indirect heating,
- at least some of the heat is brought with the aid of heat-transfer pieces, which are able to direct a grinding effect on the spodumene granules, and
- in the heating zone, the temperature of the material containing alpha-spodumene granules is kept below the agglomeration temperature of the material containing, among other things, host rock, quartz, and spar as deads.

10.

2. The method according to Claim 1, characterized in that an alpha-spodumene granule fraction, the average granule size of the granules of which is 0.5-20 mm, is fed into the heating zone.

3. The method according to Claim 1 or 2, characterized in that a first alpha-spodumene granule fraction, the average granules size of the granules of which is 0.5-20 mm, as well as a second alpha-spodumene granule fraction, the average granule size of which is 0.02-1 mm are fed into the heating zone, the first and second granules fractions being fed into the heating zone either simultaneously or consecutively.

4. The method according to any of the above Claims, characterized in that beta-spodumene is produced, which comprises granules, which pass a screen the mesh size of which is at least 0.3 mm, most suitably 0.5-1.2, typically about 0.7 mm.

5. The method according to any of the above Claims, characterized in that the beta-spodumene is recovered as product removed from the heating zone.
6. The method according to any of the above Claims, characterized in that the material removed from the heating zone is screened, in order to separate host rock and deads, such as quartz and spar, from the beta-spodumene.

7. The method according to any of the above Claims, characterized in that the heat-bringing pieces do not essentially pass a screen, the mesh size of which is 1.0 mm.

8. The method according to any of the above Claims, characterized in that the heat-bringing pieces are of metal, a ceramic material, or a rock material, the pieces are preferably of a cylindrical, cubical, spherical, or irregular three-dimensional shape.

9. The method according to any of the above Claims, characterized in that the product removed from the heating zone is screened first with a screen, the mesh size of which is at most 20.0 mm, particularly 6.0 mm or greater, and the part passing the screen is screened, after optional cooling, with a second screen, the mesh size of which is 0.3-1.2 mm, when the beta-spodumene is recovered as the part passing the latter screen.

10. The method according to any of the above Claims, characterized in that the heat-bringing pieces are separated by screening, for example, by using a screen, the mesh size of which is at most 20.0 mm, particularly 6.0 mm or greater, from the material removed from the heating zone, and are, essentially without cooling, led to heating, in order to raise their temperature to a preselected temperature, after which they are circulated for re-use in the heating zone.

11. The method according to any of the above Claims, characterized in that the beta-spodumene is cooled, before or after the second screen, to a temperature of about 100-250 °C, at which temperature it is recovered.

12. The method according to Claim 11, characterized in that the beta-spodumene at a temperature of 100-250 °C is taken to dissolution treatment, in which the lithium it contains is separated by dissolution.

13. The method according to any of the above Claims, characterized in that the heating zone comprises at least one drum kiln with a jacket, in which the material
containing alpha-spodumene granules can be heated to a temperature of 800 °C, preferably of at least 950 °C.

14. The method according to Claim 13, characterized in that heat is brought to the drum-kiln through its jacket by conduction and possibly, in addition, by radiation.

15. The method according to Claim 13 or 14, characterized in that heat produced using electrical resistances is brought through the jacket of the drum-kiln.

16. The method according to any of the above Claims, characterized in that the heating zone comprises at least one first zone, in which the temperature of the alpha-spodumene granules is raised to at least 800 °C but below the temperature required for the phase-transformation of the alpha-spodumene, as well as a second zone, in which the temperature is raised to the temperature required for the phase transformation of the alpha-spodumene.

17. The method according to Claim 16, characterized by two or more first zones, which are arranged in series.

18. The method according to Claim 16 and 17, characterized in that heat is brought to the first zone by indirect heating, for example, by using hot combustion gases as the heat-bringing medium, or by electrically-operated heating resistances.

19. The method according to any of Claims 16-18, characterized in that at least two drum-kilns arranged in series are used, when the alpha-spodumene granule fraction is first fed into the first drum-kiln forming the first zone, in which the temperature of the granules of the alpha-spodumene material is raised to at least 800 °C, when the material removed from this drum-kiln is led to the second drum-kiln forming the second zone, in which the temperature is raised to at least 950 °C.

20. The method according to Claim 19, characterized in that the second drum-kiln is divided to form at least two heating zones, when the temperature of the alpha-spodumene granule fraction is raised in stages to at least 950 °C.
21. The method according to any of the above Claims, characterized in that the alpha-spodumene of the material used contains in its crystal lattices at least some iron as an impurity.

22. The method according to any of the above Claims, characterized in that, in the heating zone, the temperature of the alpha-spodumene material and the spodumene granules it contains is kept below the agglomeration temperature of the material.

23. The method according to any of the above Claims, characterized in that, in the heating zone, the alpha-spodumene is brought to phase transformation at a temperature of 950-1080 °C, preferably 950-1050 °C.

24. The method according to any of the above Claims, characterized in that the temperature of the alpha-spodumene fed to the heating zone is about 600-900 °C.

25. The method according to any of the above Claims, characterized in that, in order to raise the temperature of 10-95 % of the alpha-spodumene to the temperature of 800 °C required for phase transformation, heat is brought to the heating zone using heated heat-transfer pieces.

26. The method according to any of the above Claims, characterized in that the phase transformation is performed in a rotary drum-kiln, in which the heat-transfer pieces direct a scraping effect to the inner wall of the drum, in order to prevent the adhesion of the spodumene material and the spodumene granules it contains.

27. The method according to any of the above Claims, characterized in that, in order to remove moisture, the material containing alpha-spodumene granules is pre-heated at about 150-400 °C before feeding to the heating zone.

28. The method according to any of the above Claims, characterized in that the material containing alpha-spodumene granules is alpha-spodumene concentrate, rough concentrate, or ground ore.
29. Apparatus for producing beta-spodumene from material containing alpha-spodumene granules, which apparatus comprises
   - a rotary drum-kiln, in which the material containing alpha-spodumene granules can be heated at a temperature of more than 800 °C in order to convert the alpha-spodumene into beta-spodumene,

characterized in that
   - in the drum-kiln there is a kiln chamber equipped with an alpha-spodumene-granule feed connection and which is surrounded by a jacket and in which there is further a beta-spodumene removal connection,
   - in the jacket of the kiln, there are means for bringing heat to the kiln through the jacket, and
   - in the drum-kiln there is a hot heat-transfer-piece feed connection, which opens into the kiln chamber delimited by the jacket, into order to feed the pieces along with the alpha-spodumene granules to be heated in the kiln, when the heat-transfer-piece feed connection is connected to an oven, in which the temperature of the pieces can be raised.

30. Apparatus according to Claim 29, characterized in that the beta-spodumene removal connection is connected to a screen, with the aid of which the pieces used to bring heat can be separated from the material removed.

31. Apparatus according to Claim 29 or 30, characterized in that the drum-kiln comprises a first zone, in which the temperature of the alpha-spodumene granules is raised to at least 800 °C but less than the temperature required for the phase transformation of the alpha-spodumene, as well as a second zone, in which the temperature can be raised to the temperature required for the phase transformation of the alpha-spodumene.

32. Apparatus according to any of Claims 29-31, characterized in that the first and second zones are thermally separated from each other by a radiation plate.

33. Apparatus according to any of Claims 29-32, characterized in that the heat-transfer-piece feed connection is connected to the conversion zone of the drum-kiln, in which the temperature can be raised to the temperature required for the phase transformation of the alpha-spodumene.
34. Apparatus according to any of Claims 29-33, characterized in that the oven, in which the temperature of the heat-transfer pieces can be raised, is arranged inside the drum-kiln, particularly it is arranged in the conversion zone of the drum-kiln.

35. Apparatus according to any of Claims 29-34, characterized in that, in the heating oven for the heat-transfer pieces, there are heating resistances connected to an electricity supply, in order to heat the heat-transfer pieces, in particular, the heating oven comprises a cylindrical jacket, in which there are heating resistances for heating the heat-transfer pieces.

36. Apparatus according to any of Claims 29-35, characterized in that, in the jacket of the drum-kiln, there is an inlet connection for the gas used for heating, and an outlet connection for the gas that has released heat, in order to bring heat through the jacket of the drum-kiln, or in the jacket of the kiln there are heating resistance connected to an electricity supply, in order to bring heat through the jacket of the drum-kiln.
# INTERNATIONAL SEARCH REPORT

## A. CLASSIFICATION OF SUBJECT MATTER

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

### INV.

- C01B33/26

### ADD.

P. B. 5818 Patentlaan 2

Rijswijk

Tel. (+31-70) 340-2040,

Fax: (+31-70) 340-3016

**Straub, Thomas**

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## B. FIELDS SEARCHED

- Minimum documentation searched (classification system followed by classification symbols): C01B

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

- **Electronic database consulted during the international search (name of database and, where practicable, search terms used)**

  - EPO-Internal, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

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**Further documents are listed in the continuation of Box C.**

**See patent family annex.**

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| * Special categories of cited documents: |
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**Date of the actual completion of the international search:**

28 June 2016

**Date of mailing of the international search report:**

08/07/2016

**Name and mailing address of the ISA:**

European Patent Office, P.B. 5818 Patentlaan 2

NL - 2280 HV Rijswijk

Tel. (+31-70) 340-2040,

Fax: (+31-70) 340-3016

**Authorized officer:**

Straub, Thomas

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