OUTOTEC LITHIUM HYDROXIDE PROCESS - A NOVEL DIRECT LEACH PROCESS FOR THE PRODUCTION OF BATTERY GRADE LITHIUM HYDROXIDE MONOHYDRATE FROM CALCINED SPODUMENE

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ABSTRACT

This paper outlines a novel development: Outotec Lithium Hydroxide Process, a proprietary technology for spodumene concentrates refining. The new process offers a fast throughput, direct leach process for spodumene concentrates to produce battery grade lithium hydroxide monohydrate product. The process is also environmentally sustainable. The process leach residue is a readily neutralized and inert mineral residue. The leach process is totally sulfate and acid free and the refining process does not involve any crystallization of unnecessary by-product salts.

The process concept is based on an alkaline leach process in two stages. Lithium is first extracted from the silicate mineral in a pressure leaching stage by soda ash. The leach reaction involves formation of sparingly soluble lithium carbonate and mineral component analcime (NaAlSi$_2$O$_6$·H$_2$O) as main components. In the second leach stage, lithium carbonate is solubilized in a conversion reaction, producing lithium hydroxide solution and solid calcium carbonate, which will report together with other mineral residues. Lithium carbonate formed in hydrothermal leaching has proven to be converted to lithium hydroxide in a fast reaction with high yields. Overall lithium leaching extraction yield from concentrate typically exceeds >90 %.

The alkaline hydroxide and carbonate processing milieu ensure very low solubilities of all the main impurity elements and compounds: Fe, Al, Si, Mg, Ca, B, P, etc. No additional impurities removal or precipitation stages are needed. Lithium hydroxide PLS is suitable feed for polishing (IX) and further crystallization of the final LiOH monohydrate product.

Outotec has successfully tested and piloted the process. Battery grade products (>56.5% LiOH·H$_2$O) have been produced from clients’ spodumene concentrate raw materials.

Keywords: Outotec, Lithium Hydroxide, Spodumene
INTRODUCTION

The ongoing boom around electric vehicles (EV) is setting the trend to lithium ion batteries development and production. The preferred chemistries for EV batteries, providing the highest energy densities, namely NMC and NCA require the lithium feed in the form of hydroxide instead of carbonate. Hence, lithium hydroxide demand growth is expected to exceed the lithium carbonate demand growth in the next few years. This is also affecting the exploitation plans of the lithium raw materials. Increase in lithium chemical prices is now speeding up the investments on the mining projects.\(^{(1)}\)

Processing hard rock mineral resources for lithium production, provides direct processing routes to lithium hydroxide. The classic route being the sulfuric acid roasting – leaching via the caustic conversion process.

These days, any new technology development for processing of natural raw materials is facing increasing sustainability and environmental requirements such as minimized chemicals consumption and easy handling of the process residues as well as process efficiency demand at the same time.

Outotec is focusing on the EV market trends providing sustainable technology solutions, covering well the whole energy metals value chain, from raw materials to end products\(^{(2)}\). Our recent technology development has been targeted to meet the market demand for the battery grade lithium salts, in particular lithium hydroxide production. Outotec has done years of extensive research and development on the alkaline leach process concept for lithium extraction from beta-spodumene. The process is based on pressure leaching of beta spodumene with soda ash for lithium extraction and recovery as lithium carbonate\(^{(3,4)}\). The alkaline process has been converted now to lithium hydroxide production. The conversion leach stage by lime produces directly a lithium hydroxide solution, which is suitable feed for polishing (ion exchange) and further crystallization of the final lithium hydroxide monohydrate product.

Outotec has tested and developed the process flowsheet and our equipment offering into a proprietary lithium hydroxide technology. Feasibility of the process has been tested and confirmed in laboratory test and pilot campaigns with clients’ concentrates.

PROCESS DESCRIPTION

Flowsheet

Outotec alkaline leach process is developed for calcined, \(\beta\)-spodumene feed. The complete lithium hydroxide process concept includes the two-stage alkaline leaching for beta-spodumene calcine to produce lithium hydroxide, followed by tailored impurities removal and crystallization of battery grade lithium hydroxide monohydrate. The process flowsheet is presented in Figure 1.
Outotec process plant will consist of the following process areas:

- Pressurised autoclave leaching of the β-spodumene calcine
- Conversion leaching of the pressure leach residue
- Leach residue filtering and handling
- Lithium hydroxide solution polishing
- Evaporative crystallization of lithium hydroxide monohydrate and product handling

**Pressure Leaching**

β-spodumene feed material is prepared into an aqueous slurry with an internally circulating sodium carbonate leach liquid. Make-up of the leach reagent sodium carbonate is fed to the leach liquid. Solid sodium carbonate is simultaneously dissolved to the hot liquid. Sodium carbonate dissolves according to following reaction:

$$Na_2CO_3(s) \rightarrow 2Na^+ + CO_3^{2-}$$  \hspace{1cm} (1)

The leach slurry is taken to a pressure leaching autoclave. In the pressure leaching, β-spodumene is leached in high pressure and temperature in an autoclave. β-spodumene reacts with sodium carbonate to form intermediate lithium carbonate and analcime solids according to the following reaction:

$$LiAlSi_2O_6(s) + Na_2CO_3 + H_2O \rightarrow Li_2CO_3 (s) + NaAlSi_2O_6 \cdot 2H_2O (s)$$  \hspace{1cm} (2)

Operating temperature in the pressure leaching is typically 200-220°C and operating pressure above 15 bar g, respectively. The effective retention time of the slurry in the autoclave is about one hour. Temperature in the Outotec OKTOP® autoclave leaching plant is controlled by direct heating with steam. High pressure steam is used for maintaining the temperature. Slurry from the autoclave is released by pressure difference into flashing tank. The purpose of the flashing is to decrease pressure and temperature from the autoclave operating conditions to atmospheric pressure and temperature in a controlled manner. Vapor generated in the flashing step is fed to pre-heating to heat the autoclave feed slurry, using a direct contact preheater. Secondary vapors in the autoclave plant are directed to an offgas scrubber.
After leaching, the slurry is fed to a filter for solid-liquid separation and simultaneous washing. Leach residues, separated with an Outotec Larox® PF pressure filtration technology, leaves this solid cake typically with about 20-23% moisture content. Leach residue consists mainly of analcime NaAlSi$_2$O$_6$ *H$_2$O, intermediate Li$_2$CO$_3$ solids, quartz & other side minerals.

Filtrate and wash filtrate contain the residual of sodium carbonate reagent. This leach liquid is circulated back to beta spodumene pulping stage.

**Conversion Leaching**

Solid cake from pressure leaching includes the intermediate lithium carbonate solids, which is converted to lithium hydroxide in a reaction with hydrated lime. Solid cakes from pressure leaching filter are first pulped with recirculating leach residue wash filtrates. The mineral slurry and milk of lime (Ca(OH)$_2$) slurry are fed to conversion step, which is done in a series of mixed atmospheric tank reactors. Lithium carbonate in the solid phase reacts with hydrated lime according to following reaction. Lithium is dissolved as lithium hydroxide and insoluble calcium carbonate is formed:

\[
\text{Li}_2\text{CO}_3(s) + \text{Ca(OH)}_2(s) \rightarrow 2\text{Li}^+ + 2\text{OH}^- + \text{CaCO}_3
\]  

Typically, lime conversion for a solid lithium carbonate feed is a slow reaction and requires high temperatures and intensive washing, in order to achieve decent > 90% lithium dissolution yields. However, the intermediate lithium carbonate solids formed in hydrothermal leaching has been reported to react very fast and effectively with yields up to 95% in only 1-1.5 hours residence time.\(^5\)

After conversion leach, the slurry is fed to final leach residue filtering and simultaneous washing. Leach residue consists mainly of analcime NaAlSi$_2$O$_6$ *H$_2$O, calcium carbonate CaCO$_3$, quartz & other side minerals. The leach residue filtered and washed in an Outotec Larox® PF pressure filtration plant, is typically left with less than 30% moisture. Leach residue is readily neutralized, and it is well suitable for disposal as landfill or some other reuse purposes.

Lithium hydroxide PLS solution after conversion is ready to be fed to lithium hydroxide crystallization process via a polishing filtration and selective ion exchange for the removal of the residual multivalent impurity cations from the solution.

The diluted wash filtrates are circulated to pressure leach cakes pulping prior to the conversion leaching stage and to preparing of the milk of lime slurry.

**LiOH PLS Polishing and Impurities Removal**

The two-stage leach process will produce directly lithium hydroxide PLS solution of very high purity. Typical Li concentration after conversion leach stage is ~10 g/l. Due to the carbonate-hydroxide milieu and a high pH, the concentrations of typical lithium process impurities (Fe, Al, Ca, Mg, P) concentrations remain very low. Al concentration is about 20 mg/L, Ca concentration about 30 mg/L and Si concentration about 50 mg/L. Soluble magnesium, manganese, iron or other heavy metals have not been not been detected above < 1 mg/l limits. The leach process is practically sulfate free. Small amount of anionic impurities, mainly chloride and sulfate will come in as an impurity of the chemicals used, in particular the soda ash feed. Hence, there is no need to do any additional impurities removal or precipitation stages. Lithium hydroxide PLS is suitable feed for polishing ion exchange (IX) treatment for the removal of the multi-valent metal cations, mainly calcium from the solution.

Ion exchange polishing for the LiOH PLS is done with a selective/chelating cation exchange resin. A resin with iminodiacetate or aminophosphonate functionality used typically e.g. in a brine softening process is suitable for the purification task. The loaded resin regeneration cycle consists of elution of the metals with excess of hydrochloric acid solution. The resin functional groups are simultaneously converted to acid form. The elution is followed by neutralization of the resin to lithium form with lithium hydroxide solution. There are washing steps inbetween the loading, elution and neutralization steps. The acidic eluate is fed to a separate effluent neutralization and treatment process.
LiOH Crystallization

Lithium hydroxide monohydrate product is crystallized from the lithium hydroxide solution by means of pre-concentration, followed by the vacuum crystallization process.

In the crystallization product salt Lithium hydroxide LiOH·H2O is crystallized according to following reaction:

\[ \text{Li}^+ + \text{OH}^- + \text{H}_2\text{O} \rightarrow \text{LiOH} \cdot \text{H}_2\text{O}(s) \]  

(4)

One to two crystallization stages in series is needed for battery grade (>56.5% LiOH) product quality. The soluble alkali metal cations (Na, K) target levels in the final product define the crystallization process requirements and parameters.

Crystallization mother liquid contains the entrainment of all soluble impurities from the two-stage leach process. Mother liquid is circulated back to crystallization feed. Some small portion of the mother liquor is fed to bleed treatment. Feed rate to bleed treatment is determined by the maximum soluble impurity concentrations (mainly Na⁺, K⁺) in the crystallization circuit.

METHODOLOGY

The process was tested in a bench scale pilot at Outotec Research Center in Pori, Finland. The pilot was carried out in semi-continuous manner, where solutions would progress through process stages operated in batch set-up. The test work consisted of soda pressure leaching, conversion leaching for lithium hydroxide solubilization, followed by solid-liquid separation and washing for the leach residue. Lithium hydroxide solution was purified by ion exchange and fed to lithium hydroxide monohydrate crystallization in one crystallization stage.

Materials

Two calcined spodumene concentrates were used as raw materials in this test work. The calcination part of the pilot was carried out in Outotec Research Center in Frankfurt, Germany. The calcination was a continuous process in a fluidized bed calciner at 1050 °C, with a feed rate of 10-12 kg/h. The Li₂O contents of the concentrates were 6.52% (Calcine 1) and 6.63% (Calcine 2), while other major constituents of the samples were silica (67.2% and 65.7%) and alumina (25.12% and 24.75%). The primary minerals found in both calcine samples were spodumene, albite, potassium feldspar, quartz, and muscovite. The only Li containing mineral in the concentrates was spodumene. According to XRD analysis, spodumene β-conversion of 73.8% and 86.5% were achieved for Calcine 1 and Calcine 2 respectively, while total conversion was 95.9% for Calcine 1 and 96.6% for Calcine 2. γ-spodumene/virgilite was found in both samples, 19.7% in Calcine 1 and 9.2% in Calcine 2. By wet sieving, Calcine 1 was determined to have a D₈₀ of 102 µm and Calcine 2 a D₈₀ of 89 µm.

Equipment

Soda leaching was carried out in a 1-gallon (3.78 liters) stainless steel autoclave. The autoclave had internal cooling coils and the autoclave shell was electrically heated. Concentrate and soda ash were weighed, and soda was dissolved in circulated filtrates from the previous soda leaching batches. Concentrate and soda solution were mixed into a slurry and if necessary the pH of the slurry was adjusted to 11.5 by addition of 500 g/l NaOH-solution. The slurry was added to the autoclave, which was sealed, and mixing and heating were started. The slurry volume was 2.8 liters, leaching time was 1.5 hours and temperature was 220 °C. After reaction time, the slurry was cooled down to room temperature and removed from the autoclave. The slurry was filtered, and the leach residue was washed with water after which it proceeded to the LiOH conversion stage. Filtrate and cake wash waters were recycled to slurry preparation stage.

Lithium hydroxide conversion leaching was carried out in an inert atmosphere, in a 5 liter stainless steel reactor equipped with a mixing unit, as well as temperature and pH measurement. Soda
pressure leach residue and calcium oxide were weighed. Calcium oxide was dissolved in circulated leach residue wash filtrates. Soda leach residue and milk of lime slurry were mixed to a process slurry and added to a reactor and stirring was started. Slurry volume was 3 liters, and the conversion reaction was carried out for 2 hours at ambient temperature. After reaction time, the slurry was removed from the reactor and filtered, and the residue was washed with water and discharged.

The filtrate from LiOH conversion leach stage was purified with ion exchange resin loaded in a fixed bed column. Lanxess’s Lewatit® MDS-type resins TP 207 and TP260 were both tested in the purification step. Afterwards, LiOH-H$_2$O was crystallized batch-wise from the solution by vacuum evaporation.

**Analysis**

Solution samples were analyzed with ICP-OES (inductively coupled plasma optical emission spectrometer) for metal ion concentration. Solid samples were analyzed with either ICP-OES or ICP-MS (inductively coupled plasma mass spectrometer) after total dissolution or fusion melt for metal concentration, whereas carbon and sulfur concentrations were analyzed with an Eltra CS-2000 automatic analyzer. Chloride concentrations of solid samples were measured by a pyrohydrolysis method and silica was analyzed colorimetrically using a Hach DR 5000 UV-Vis spectrophotometer.

**Calculation of Li-extraction**

Li extraction in the LiOH conversion stage was calculated with Equation 5, since aluminium does not dissolve during leaching.

\[
\text{Li- \% (Al)} = 100\% - \left( \frac{\% \text{ Li sample}}{\% \text{ Al sample}} \cdot \frac{\% \text{ Al feed}}{\% \text{ Li feed}} \cdot 100\% \right)
\]  

(5)

**RESULTS AND DISCUSSION**

Solids concentration in soda leaching was 250 g/l. An excess of soda was used in each leaching test and the dosage was adjusted according to the Na concentration in the soda leach filtrate, with the goal of having 3-4 g/L of Na in the filtrate. The concentrations of Li, Na, Si and K in solution samples from soda leaching are shown in Figure 2. Li concentration was approximately 2 g/l, which is the solubility of lithium carbonate. Na concentration ranged between approximately 1.2 and 5.5 g/l and varied according to the soda dosage. Other major elements found in the solution samples were Si and K, with concentrations between 100 and 1000 mg/l. It could be seen from the solution analysis, that K concentration was following the same trend as the Na concentration, which was due to potassium taking part in the soda leach reaction. This could be seen during limitations of Na availability, especially at around 100 hours of pilot operation, when both metals' concentrations in soda leach filtrate were at their minimum. The extraction of other metals, such as Ca, Fe, Mg and Mn was minimal, with their concentrations mostly being under detection limit 10 mg/l, while Al concentration after soda leaching was under the detection limit 20 mg/l.
The percentage lithium extraction to lithium hydroxide solution, after the two-stage leaching, calculated with equation 1 is shown in Figure 3. The extraction was on average 91%, with values ranging from 84% to 94%. Calcine 1 was used until 112 hours of pilot operation and Calcine 2 was used between 112 and 272 hours. At the end of the pilot, Calcine 1 was used again. The solids concentration in the conversion leach stage was approximately 300 g/l throughout the pilot. In general, slightly higher Li extractions were achieved with Calcine 2 than with Calcine 1, most probably due to a higher beta-spodumene conversion stage in the material Calcine 2. Steady > 90% lithium extraction recovery was obtained when leaching reagent sodium was maintained at the target level. The solid residue from the conversion leach stage was detected to consist mainly of analcime and calcium carbonate minerals.
The lithium hydroxide product solution from the conversion leach stage, which contained approximately 8-10 g/L of Li, was purified with a cation exchange resin and used as feed solution to lithium hydroxide monohydrate crystallization. The impurity levels of the purified solution can be seen in Figure 4. The concentration of Ca was mostly under detection limit 10 mg/L, whereas Mg was under detection limit 1 mg/L. Al concentration ranged from 10 to 50 mg/L. Si and K concentrations followed each other until 224 hours of pilot operation, with concentrations ranging from 20 to 100 mg/L. At the end of the pilot, Si settled to approximately 30 mg/L, while K concentration ranged from 90 to 170 mg/L. Na concentration was varying the most, with concentrations between 180 mg/L and 1100 mg/L. However, due to absence of sulfate ions in the process, sodium co-crystallization with lithium hydroxide is limited. Hence, Na concentration in the product crystals remained quite consistent, regardless of the sodium level in crystallization circuit. Instead, the sodium level was mostly dependent on proper washing of the product crystals.

The solution purified by ion exchange was fed to the lithium hydroxide crystallization stage, where lithium hydroxide monohydrate was crystallized in a single-stage batch operation. After the crystallization, the crystals were filtered and washed with a concentrated LiOH solution. The typical impurity profile of the produced crystals is shown in Table 1. The products were high purity, with concentrations of most metallic and anionic impurities being <20 ppm or lower. This impurity profile represents a battery grade product with >56.5% LiOH.

**Table 1. Typical analysis of the product LiOH·H2O crystals in Outotec process piloting.**

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The filtrate, or mother liquor, received from the crystallization was a concentrated LiOH solution containing the entrained soluble impurities, such as Na, K, Si and Al. Impurities were bled from the crystallization circuit as a side stream. Bleed treatment involves lithium precipitation as Li₂CO₃. The soluble impurities will remain in the liquid. These solids and liquids were fed upstream to the leach process.

CONCLUSIONS

A novel lithium hydroxide process concept was developed, consisting of a two-stage alkaline leaching for beta-spodumene calcine to produce lithium hydroxide, followed by impurities polishing by IX and the crystallization of lithium hydroxide monohydrate.

Process viability was demonstrated in a bench scale pilot, carried out in semi-continuous manner, where solutions would progress through process stages operated in batch set-up. The feed materials for the pilot were two calcine samples with 6.52% (Calcine 1) and 6.63% Li₂O content, produced in a continuous fluidized bed calcining pilot. Spodumene β-conversion was 73.8% and 86.5% for Calcine 1 and Calcine 2 respectively, while total conversion was 95.9% for Calcine 1 and 96.6% for Calcine 2. Lithium leaching performance was monitored by the solid analyses from leach residue. The lithium extraction yield was on average 91 %, with highest values up to 94 %. The leaching performance was mostly dependent by the leaching reagent sodium carbonate level in the leach liquid as well as the feed material β-conversion degree, which was somewhat higher for Calcine 2. The process leach residue is readily neutralized and inert mineral residue, consisting of mineral analcime and calcium carbonate as main components, plus the side/gangue minerals.

Impurities levels was monitored in the process liquids: the circulating sodium carbonate leach solution in the pressure leach stage and the lithium hydroxide solution produced in the conversion leach stage and fed to the crystallization process. The alkaline hydroxide and carbonate processing milieu ensured very low solubilities of all the main impurity elements and compounds: Fe, Al, Si, Mg, Ca, B, and P. Product quality was monitored by product lithium hydroxide monohydrate analysis. The product obtained in one crystallization stage was of high purity, with concentrations of most metallic and anionic impurities being <20 ppm or lower. This impurity profile represents a battery grade product with >56.5% LiOH.

REFERENCES