Monitoring and Controlling of Conversion Degree from **α**- to **β**-Spodumene in High-Temperature Calcination Process with **Timegated® Raman Spectroscopy**

Case Study:
Keliber Lithium Project in Finland

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The global lithium market is growing strongly due to development of new technologies and energy sector, mainly because of the increased use of lithium-ion batteries for automotive and domestic applications. More and more hybrid and electric vehicles, energy storage systems and portable devices are available on the market and the demand for lithium grows accordingly. Furthermore, the shift to better performing Lithium-ion batteries in emerging and developing countries increase the demand for lithium. Australia, Chile, Argentina and China dominate the world lithium supply, but new sources are required to meet the growing demand.

Keliber Oy is developing their Li project in Kaustinen, Central Ostrobothnia in Finland. According to the Pre-Feasibility Study (PFS) completed in March 2016 the project is profitable and all the financial figures are positive. The drilling program, conducted during summer 2016 and winter 2017, increased measured and indicated mineral resource estimates by 2,08 tonnes (35%). The project is targeting to start the production from the biggest spodumene deposits in Europe. Keliber is currently preparing the Definite Feasibility Study aiming to produce 9000 tonnes lithium carbonate annually. The production is estimated to start early 2020.

Spodumene conversion enables efficient lithium extraction

Spodumene ($LiAlSi_2O_6$) is a monoclinic pyroxene mineral. Pyroxenes, incl. spodumene exhibit various lattice symmetries. Pyroxenes undergo various phase transitions under high pressures and temperatures. Spodumene has three polymorphic forms: monoclinic pyroxene α-spodumene, tetragonal β-spodumene, and hexagonal Υ-spodumene. Only α-spodumene exist naturally except for some extreme volcanic conditions. The α-spodumene form is closest to a stable pyroxene structure and the transition from α to β form requires high temperatures. The conversion from α to β spodumene form makes the subsequent lithium extraction procedures easier by making the mineral material more reactive. The conversion increases the volume and surface area of the material, increases the mobility of lithium species and weakens the spodumene crystal structure.

Historically Raman spectroscopy has suffered from prominent fluorescence interference in many applications. However, techniques like time-gating have enabled the use of Raman spectroscopy even in many demanding applications where other analysis methods are not as effective. Timegated® Raman spectroscopy makes it possible to measure highly fluorescent and hot materials.

Timegate Instruments Ltd measured spodumene conversion rate during batch kiln furnace tests in May 2017 (see Figure 1). In this case α-spodumene concentrate was heated up to 1025 – 1075°C temperature. Spodumene conversion from α- to β-form occurs in this temperature range. Samples from the process were taken every 5 minutes and the conversion degree was detected with a Timegate Raman spectrometer setup (see Figure 2). The conversion degree was calculated using peak heights of 707 cm^{-1} (α-spodumene) and 500cm^{-1} (β-spodumene) Raman signals.

The Timegated® Raman spectroscopy has also been tested with spodumene slurries and it has shown very positive results also providing a potential for on-line analysis of spodumene in minerals processing, too. An effective analysis method for α- and β-spodumene quantification is needed for efficient conversion parameter optimization. Analysis methods for lithium or spodumene measurements include MLA, XRD, XRF, LIBS and hyphenated ICP-techniques; but only XRD can be used for α/ β form quantification. In many cases a comprehensive analysis requires a combination of these aforementioned techniques mentioned before.

Figure 1: Batch kiln furnace

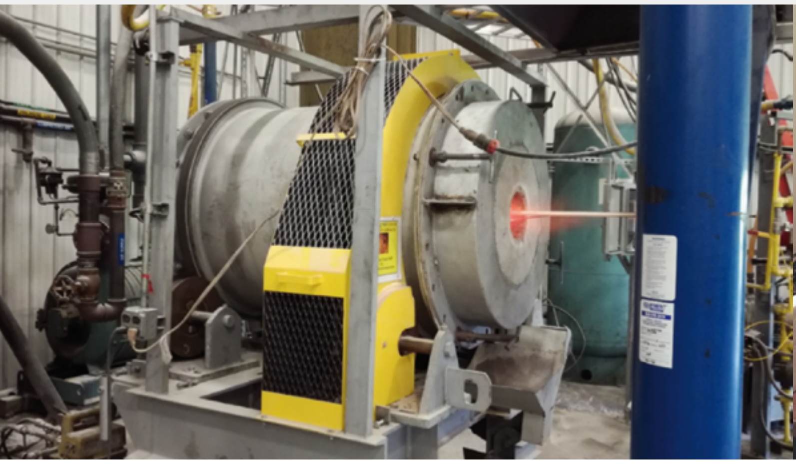


Figure 2: The Timegate Raman setup

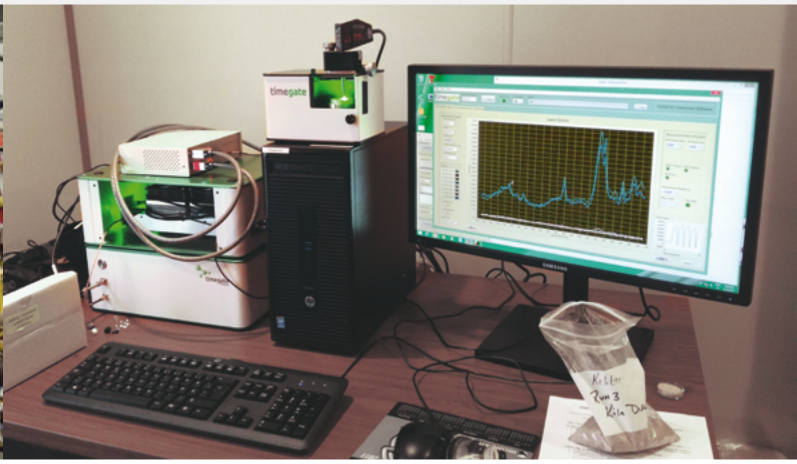


Table 1: Conversion ratio over time

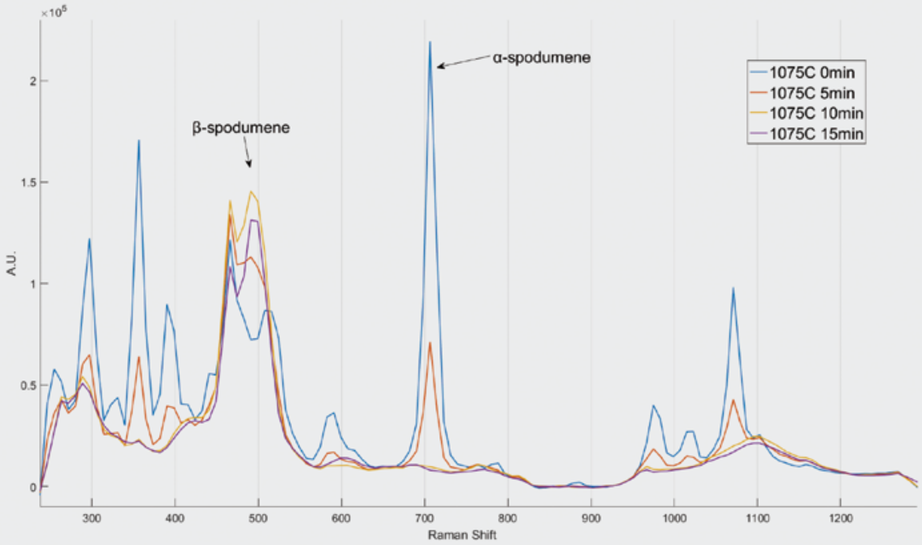
Time	Calculatory β-conversion degree [m-%]
0 min	35.1%
5 min	80.6%
10 min	99.8%
15 min	100%

Batch kiln furnace tests proved Timegated® Raman spectroscopy to perform well with detecting the conversion degree from α- to β-spodumene. Figure 3 and Table 1 show a test run with four samples taken every five minutes after the furnace reached a temperature of 1075°C. The samples taken from the process were analysable after a short cooling down period and thus fast feedback from the process was obtained.

Table 1 indicates the calculatory β-conversion degree at each point in time. The detection limit is about 1% which equals to a minimum of 95% conversion degree. As the measurement results indicated, conversion was completed after about 15 minutes. The same can be seen in Figure 3 where the 700cm^{-1} α-spodumene Raman signal intensity decreased throughout the test run while the β-spodumene 500cm^{-1} signal intensity increased as the spodumene conversion proceeded.

Raman spectroscopy can be used for on-line and at-line applications and it offers a non-destructive analysis method that requires minimal amount of sample preparation. Automated and fast analysis methods enable effective process control and feedback which in turn help with optimizing process parameters like α- to β-spodumene conversion time and temperature.

Figure 3:
Test run for α-spodumene conversion to β-spodumene.



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