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A REVIEW: THE BENEFICATION OF LITHIUM MINERALS FROM HARD ROCK DEPOSITS

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ABSTRACT

Lithium is a silver-white alkali metal that has recently become a target commodity for many junior mining companies. Lithium has a wide range of applications including ceramics and glass, lubricating greases, air treatment, continuous cast mold flux powders, polymer production, and primary aluminium production, but the current popularity of lithium can be attributed to an anticipated increase in demand for lithium ion batteries. The most common lithium-bearing minerals occur globally in pegmatites and granites. Spodumene [$LiAl(Si_2O_6)$)] is the most desirable economic lithium-bearing mineral due to its high lithium content (theoretical Li_2O content of about 8 wt%). However, lithium can also be hosted in petalite, micas, tourmaline, and phosphate minerals. In Canada there are a number of spodumene deposits in Ontario and Quebec at development stage that have the potential to help narrow the forecast lithium supply gap stemming from the widespread acceptance and use of electric vehicles. This paper discusses the beneficiation of hard rock lithium deposits, including an in depth review of the use of flotation to upgrade spodumene. A review of the use of dense media separation (DMS), magnetic separation, and roasting as means to process spodumene bearing ores is also discussed.

INTRODUCTION

Lithium is a soft, silver-white alkali metal with atomic number 3. As of 2015, the end use of lithium was estimated to be as follows: lithium-ion batteries (35%), ceramics and glass (32%), lubricating greases (9%), air treatment (5%), continuous casting mould flux powders (5%), polymer production (4%), primary aluminium production (1%) and other uses (9%) (Jaskula, 2014). Lithium is found in brine lake deposits containing lithium chloride and in hard rock pegmatite deposits. It can be sold in a range of product types; as mineral concentrate, brine, compound (lithium carbonate or lithium hydroxide) and metal depending on its intended end use (Goonan, 2012; Jaskula 2014).

In the 1990s the United States and Chile were the largest producers of lithium globally, primarily from brine operations (Ober, 1994). Most of the lithium compounds produced over this period were consumed in the glass, ceramics and aluminium industries. In the 1980s and 1990s there were two major lithium operations in the United States: brine operations at Silver Peak, Nevada, and a spodumene mine and lithium carbonate/lithium hydroxide plant in Kings Mountain, North Carolina. The Kings Mountain operations ceased production in 1991 and were eventually dismantled in 1994. Brine operations were also active in Argentina and Chile, while the largest lithium ore deposit in the world was operated at Greenbushes, Western Australia. During this period it was predicted that major shifts in demand for lithium would come from the success and widespread use of electric vehicles (Ober, 1994).

Lithium is still produced from the brine operations at Silver Peak, NV, but in more recent years Chile has become the world's leading producer of lithium carbonate from brines. Australia has maintained its position as the world's largest producer of lithium mineral concentrate, the majority of which is exported to China to produce lithium carbonate and lithium hydroxide (Jaskula, 2014). A spodumene concentrate was also produced at the Tanco Mine in Manitoba, Canada beginning in the 1980s through to 2010 when lithium operations were suspended due to fluctuations in lithium market price (Martins et al., 2013).

Lithium has recently become a commodity of great interest in the mining industry for junior miners and large capitalisation miners alike. The growing use and acceptance of electric vehicles has led to forecasts that if 100% of the 60 million cars produced per annum globally were to be replaced by plug-in hybrid vehicles, as some predict will occur >2050 (Gaines and Nelson, 2009), then lithium carbonate demand would increase to ~5 times current production levels (Goonan, 2012). While this is a simplistic and extremely high estimate, this possibility has led to an increase in junior lithium mining company activity, particularly among those with an aim to develop hard rock lithium deposits in Canada and Australia (Morgan Stanley, 2015).

Listed lithium companies have been deemed a top investment pick over the next three years by major financial firms such as Morgan Stanley (Morgan Stanley, 2016) due to the increased demand for lithium-ion batteries in electric vehicles and short term supply shortages. Junior mining and exploration companies are quickly working to fill the current lithium supply shortage. However, the development of new lithium operations will not be without significant challenges. Other estimates by Clarke (2013) suggest that if existing lithium producers operate at their current capacities and all expected new producers come online, there will be a surplus of supply. This indicates that the lithium market only has room for those new deposits with superior project economics to come into production in the coming years.

This paper focuses on one of the key challenges encountered in the development of hard rock lithium deposits: the beneficiation methods used to upgrade spodumene ores to produce concentrate suitable for lithium extraction by hydrometallurgical operation. . This paper includes an in depth review of the use of flotation to upgrade spodumene as well as a review of the use of dense media separation (DMS), magnetic separation, and roasting in spodumene processing. A critical assessment of past research in the area is made with the objective to identify areas for improvement and increase the economic viability of greenfields hard rock spodumene deposits.

MINERALOGY

As mentioned in the previous section, there are two economic lithium deposit types: brine and hard rock ore. While brines that contain commercially viable concentrations of lithium are not common, the extraction and processing of brines is associated with relatively low capital costs and is far less energy intensive than extraction of lithium from hard rock ores (Clarke, 2013). Brines rich in lithium chloride, such as those found in the Atacama Desert of Chile and near Silver Peak in Nevada, are pumped from the ground through evaporation ponds and are concentrated by means of solar evaporation, from levels as low at 300ppm Li to more than 6000ppm Li over a period of 18 months. When the concentration of lithium in the brine is sufficiently high, the brine is used to produce a lithium carbonate product (Ober, 1994).

The extraction of lithium from hard rock deposits is a far more complicated and energy intensive process. There are more than 30 lithium bearing minerals; however lithium is mined from five major minerals: spodumene, amblygonite, zinvaldite, petalite and lepidolite (Bulatovic, 2014). Of these, spodumene is the most prevalent

economic lithium bearing mineral (Ober, 1994). It is an alumino-silicate mineral with the chemical formulae $Li_4Al_4[SiO_3]_8$, composed of silica tetrahedral bound laterally through ionic bonding with lithium and aluminum in octahedral co-ordinations (Gasalia, et al., 1987). It is tabular, extremely hard and insoluble in dilute acids (Bulatovic, 2014). Each crystallographic plane of spodumene has a different number of Al sites, and broken Al-O bonds per Al site. It has been found that the surface potential of spodumene is governed by {110} (cleavage/side planes) and {001} (end planes) crystal planes of the columnar crystal particles, which have the highest density of Al sites in comparison with other crystalline planes (Moon and Fuerstenau, 2003). **Figure 1** shows an image of spodumene grains from a flotation concentrate.
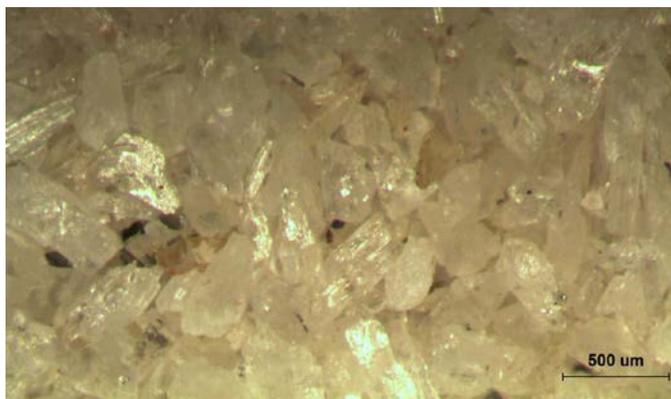

Figure 1. Spodumene grains (Image from SGS Lakefield).

Spodumene occurs in pegmatite deposits along with other silicate minerals such as feldspars, micas, and quartz (Norman and Gieseke, 1940; Browning, 1961; Redeker, 1981; Baleand May, 1989; Amarante et al., 1999; Clarke, 2013; Bulatovic, 2014). There are three types of spodumene that can occur including phenocrystic spodumene in un-zoned pegmatite with a Fe_2O_3 content of 0.6-0.9% (often from iron substituted in the spodumene crystal structure), zonal spodumene with a Fe_2O_3 content of 0.01-0.03%, and spodumene plus quartz aggregates psuedomorphous after petalite with and Fe_2O_3 content of 0.007-0.03%. Primarily the first type of spodumene is found in deposits that can be economically mined (Heinrich, 1978). Spodumene bearing pegmatite deposits range in lithium head grade, from 1% Li_2O in low grade deposits to as much as 4% Li_2O in higher grade deposits (Clarke, 2013).

Quantitative mineralogy using QEMSCAN, X-ray diffraction anlaysis, mineral chemistry including electron microprobe and Laser Ablation (LA) Inductively Coupled Plasma Mass Spectrometer (LA ICP-MS), are commonly used to determine the mineralogical attributes (liberation, grain size, chemistry of spodumene and other Li-bearing minerals).

OBJECTIVE OF SPODUMENE BENEFICIATION

Spodumene is upgraded with the objective to produce either chemical grade or ceramic grade concentrate, depending on its intended end use. The type of concentrate is also dictated by the impurities in the spodumene crystal structure, mainly iron, as well as the size distribution. The purity specification for spodumene concentrates depends on the specific end use. **Table 1** shows a summary of specification data for spodumene concentrates including recent concentrate specifications for two different ceramic grade concentrates from Rockwood Lithium (2015) and historical concentrate specifications for ceramic grade concentrate produced by the Foote Mineral Company and chemical grade spodumene concentrate produced by the Lithium Corporation of America, as originally reported by Redeker (1979). Concentrate assays from other spodumene processing operations globally have been summarized by Bulatovic (2014).

For ceramics and glass, a coarser concentrate is required with a high Li_2O content and a relatively low gangue mineral content. The low iron requirements in particular make concentrate contamination by iron silicate bearing minerals, such as amphibole and pyroxene,

problematic. Size distribution and purity specifications are not as strict for chemical grade spodumene concentrate and some gangue impurities are allowable, making it possible to obtain higher processing recoveries (Redeker, 1979).

Table 1. Purity specifications for ceramic and chemical grade spodumene concentrates (Redeker, 1979; Rockwood Lithium, 2015).

Assay (%)	Ceramic Grade SC7.5[1]	Ceramic Grade SC6.5[1]	Ceramic Grade[2]	Chemical Grade[2]
Li_2O	7.5	6.5	6.76	5.60-6.50
Fe_2O_3	0.1	0.25	0.73	1.45-3.00
SiO_2	62.5	-	63.3	62.0-66.0
Al_2O_3	25.0	-	26.6	24.6-26.1
Na_2O	0.35	-	0.45	0.53-0.70
K_2O	0.2	-	0.69	0.72-1.40
CaO	0.1	-	0.18	-
P_2O_5	0.25	-	0.34	-

[1] Rockwood Lithium (2015)
[2] Redeker (1979)

BENEFICIATION OF HARD ROCK DEPOSITS

Dense Media Separation

Dense Media Separation (DMS), also known as Heavy Media Separation (HMS), is a pre- concentration process commonly used to reject gangue minerals prior to grinding for final liberation. It employs the use of a heavy medium to separate products of varying density. Depending on the density of the media used, particles with a higher density will sink, while lower density particles will float (Wills and Napier-Munn, 2005).

In relation to spodumene beneficiation, DMS can be used to separate spodumene from lighter silicate minerals in a pre-concentration stage. Spodumene has a reported specific gravity between 3.1 and 3.2, while quartz and feldspar have specific gravities between 2.5 and 2.6, and mica has a specific gravity between 2.8 and 3.0. Thus, the separation of these minerals by dense media is possible. However due to the close relative densities, spodumene liberation must be high at larger particle sizes in order to minimize lithium losses to the float product. Iron bearing silicates such as amphibole tend to have higher densities (2.9-3.2), and are therefore notseparated from spodumene through dense media separation. Typically DMS is conducted on the +500-850 µm fraction, with the undersize feeding a flotation circuit. In some cases, a middlings DMS product containing unliberated spodumene associated with silicate gangue is combined with the undersize to feed the flotation circuit.

DMS was used for a period of time at the two plants operating in the Kings Mountain area of North Carolina. The Foote Mineral Company ran a gravity plant from the 1950s through to the 1960s consisting of a 3 meter Wemco cone separator operating at a S.G. cut of 2.62, and a second cone separator operating at an S.G. cut of 2.92 to make chemical grade concentrate and enriched feed for spodumene flotation (Redeker, 1979).

The Lithium Corporation of America began using DMS to concentrate spodumene at their Kings Mountain operations in the late 1960s. The separators were operated at S.G. cut points of 2.7 and 2.8 on -10mm/+212µm feed. The DMS circuit was successful in upgrading the ore from 1.3% Li_2O to 3.5% Li_2O with 50-60% Li recovery. Due to issues with washing and screening, the DMS feed size was increased, which led to lower lithium recoveries. As a result of low lithium recoveries all DMS operations at Kings Mountain were decommissioned in the early 1970s and flotation was solely used to upgrade spodumene (Redeker, 1979).

DMS was tested on an ore containing K-feldspar, quartz and muscovite mica from northern Portugal at the laboratory scale tests on four separate size fractions: -6.7/+4.75mm, -4.75/+3.35mm, -3.35/+2.36mm and -2.36/+2mm. The final sink products contained 5% Li_2O with lithium recovery between 39% and 61%. Overall it was determined that better lithium recovery could be obtained on size fractions less than 4.7mm due to improved spodumene liberation (Amarante, 1999). Bulatovic (2014) also outlines the successful use of

DMS in the processing of ore from Bernic Lake, Manitoba, Canada, where it was possible to reject ~36% of the mass into the float product with lithium losses of only 3.1% at a feed size of -12mm/+0.5mm at an S.G. cut point of 2.7. The use of DMS as a means to separate spodumene from silicate gangue minerals has also been reported by Aghamirian et al. (2012).

In summary, DMS can be an effective means to pre-concentrate spodumene from hard rock operations with the benefit of less feed to the grinding and flotation circuits and subsequent capital, energy and operating cost savings. However, the effectiveness of DMS is highly dependent on the degree of spodumene liberation at coarse particle sizes. Poor spodumene liberation will result in significant lithium losses to the float product and negate economic justification for its use.

Ore Pre-Treatment

Historically, research has demonstrated that spodumene flotation is more efficient after first 'cleaning' the mineral surfaces. The first reported study on this was conducted by Norman and Gieseke (1940) and similar findings were later reported by Manser (1975). The authors conducted flotation testwork on a number of different ores from across the United Sates (Kings Mountain NC, Lincolnton NC, Warren ME, Tinton South Dakota and Dixon New Mexico). They found that in order for flotation to be selective, it was necessary to first 'clean' or 'scrub' the pulp using one of Na_2SiF_6, Na_3PO_4, Na_2S or NaOH. The use of NaOH either alone or with Na_2S was found to be the most suitable. The more weathered the material was, the more cleaning was required for selective flotation.

The practice of cleaning the ore prior to spodumene flotation was practiced at the Kings Mountain operations where 225 g/t NaOH was added to the grinding mill to help activate spodumene (Redeker, 1981). Laboratory and pilot plant testing was undertaken to eliminate the use of NaOH at Kings Mountain and replace it with a combination of lignin sulphonate and sodium fluoride (Browning, 1961). While this reagent substitution was reported to be successful, subsequent reports (Redeker, 1979; Redeker 1981) indicated that NaOH continued to be used as the primary reagent in cleaning.

Bulatovic (2014) outlined two methods of pulp pre-treatment. The first was conditioning the pulp with NaOH at 50-60% solids for 20-30 minutes, similar to the practice described above, and the second was treatment with Na_2S under similar conditions as an alternate option, yielding similar flotation performance. Moon and Fuerstenau (2003) attributed enhanced spodumene flotation recovery after treatment with NaOH prior to flotation to a breakdown of structural silica tetrahedral or re-adsorption of dissolved aluminum species, exposing more aluminum sites on the surface of the spodumene for collector adsorption.

De-sliming

Following pre-treatment, it is common practice to de-slime the ore prior to flotation. Without de-sliming it may be difficult to achieve selective flotation of spodumene from its associated gangue minerals. This is done using hydrocyclones, the cut size for which is dictated by the desired size distribution of the flotation concentrate and the spodumene liberation in the ore.

At Kings Mountain, it was reported that after grinding to 100% passing 210μm, 37μm slimes were removed by hydro cyclone, scrubbed, diluted and de-slimed again. All slimes were then de-slimed at 15μm. The plus size from this de-sliming stage was combined with +37μm material for flotation (Redeker, 1981). The slimes contained 7.4% of the weight, assayed 1.43% Li_2O, and were associated with 6.5% Li losses. Similarly, at the Greenbushes operation in Western Australia, cyclones are used to remove the -20μm material prior to flotation (Bale and May, 1989).

Flotation

Flotation is a widely used and effective means to upgrade spodumene from pegmatite deposits. The flotation of spodumene will be covered in three sections: flowsheet configuration, reagents, surface chemistry, and the effect of metal cat-ions. These aspects will be discussed in terms of current practice and new research.

Flowsheet configuration

There are several flotation flowsheet options, the selection of which depends on the nature of the gangue minerals present. These options include:

1. Spodumene flotation only (Bulatovic, 2014; Baarson et al., 1961)
2. Reverse gangue flotation (mica) followed by spodumene flotation (Bulatovic, 2014; Baarson et al., 1961)
3. Spodumene flotation followed by reverse gangue flotation (mica) on the spodumene circuit tailings (Redeker, 1979)
4. Reverse gangue flotation (mica) followed by spodumene flotation and then reverse feldspar flotation from the spodumene flotation tailings (Bulatovic, 2014; Browning, 1961).

Presently, production of spodumene from hard rock deposits is dominated by the Greenbushes operation in Western Australia. While insight can be gained from examination of the details reported on the beneficiation of hard rock spodumene ores from Kings Mountain, NC, and Tanco, Manitoba, it is important to note that these deposits are not currently in operation.

Reagents

Mica Flotation. Typically, the reagents used in reverse silicate gangue mineral flotation are the same regardless if the reverse flotation stage is performed before or after spodumene flotation. Reverse gangue mineral flotation typically includes mica flotation, to avoid significant quantities of mica in the final spodumene concentrate. Mica is undesirable in ceramic raw material because it causes brown specks after firing (Norman and Gieseke, 1940). Mica flotation is often conducted in acidic pulp conditions (pH 2-2.5) using H_2SO_4 as a pH modifier and an amine based cationic collector (Browning, 1960; Bulatovic, 2014). Redeker (1981) also reports use of petroleum sulphonate to float mica, also under acidic pulp conditions. Mica pre-flotation offers the added benefit or removal of iron silicates and reducing the overall iron content of the final spodumene concentrate, at least in part. In some instances these minerals may float to some extent with the mica using an amine collector in acidic pulp (Norman and Gieseke, 1940).

There are also collectors that are capable of selectively floating mica from spodumene under alkaline conditions. Aero 3030C from Cytec is an example. This particular collector is composed of amines, tallow alkyl acetates and ethyl hexanol (Gaied and Gallala, 2011). This may be beneficial as spodumene is also carried out under slightly alkaline conditions and there is no need for major pulp pH modification. Baarson et al. (1961) reported the use of Dextrin as a spodumene depressant in flotation of mica under alkaline conditions.

Feldspar Flotation. In some instances feldspar is floated from the spodumene circuit tailings and sold as feldspatic sand to glass companies. In order to float feldspar from the primarily quartz tailings, hydrofluoric acid (HF) is used to condition the pulp and adjust pH to ~2-2.5. Feldspar is then floated using a tallow amine acetate collector with a 12-14C hydro carbon chain length, kerosene and frother (Redeker, 1981). If there is mica present in the ore, it must be removed prior to feldspar flotation otherwise it will report to the feldspar concentrate, making the product unsuitable for ceramics and glass applications (Norman and Gieseke, 1940). In some cases, it is necessary to separate K-Feldspar from Na-Feldspar as K-Feldspar can contain large concentrations of rubidium (>1%) in its crystal structure, making it more valuable for use in durable ceramic products (Martins et al., 2013). K-Feldspar can be preferentially upgraded by adding NaCl during feldspar flotation. The final tailings from feldspar flotation can be a high grade quartz concentrate with an assay > 98% SiO_2.

Extensive studies have been conducted on the flotation of silicate minerals such as mica, quartz and feldspars, including work by Pradip and Fuerstenau (2005). The details of this flotation process will not be review in great detail in this paper.

Beryl Flotation. At Kings Mountain in North Carolina, beryl was also found to occur with spodumene. To upgrade beryl, first the spodumene was floated using a fatty acid collector. The spodumene

tailings were then conditioned with sulphuric acid and an amine collector for mica rejection. The mica flotation tailings were then thickened and conditioned with hydrofluoric acid and then washed. The pulp was then conditioned with NaOH and beryl was floated using oleic acid to produce a beryl concentrate assaying 3% Li_2O and 1.57% BeO with 75% beryl recovery (Browning, 1961).

Spodumene Flotation. The following is a comprehensive list of collectors that have been tested on real ores and pure minerals for the flotation of spodumene (Table 2):

Table 1. List of collectors tested on spodumene ores.

Collector	Reference
Tall oil fatty acid (5-7% rosin acid content)	Redeker (1981)
Oleic acid, sodium and ammonium oleate, and different sulphate/sulphonated/phosphorated fatty acids	Norman (1940)
Oleic acid	Yu et al. (2015)
Oleic acid	Amarante et al. (1999)
Oleic acid + naphthenic acid	Amarante et al. (1999)
Sodium oleate	Xu et al (2016)
Sodium oleate + dodecyl trimethyl ammonium chloride	Xu et al (2016)
Dodecylamine	He et al. (2014)
LR15: 62% Oleic acid, 27% petroleum sulphonate, 8% kerosene, 8% pine oil	Bulatovic (2014)
LR17: 61.6% D30LR, 27.7% petroleum sulphonate, 8.2% kerosene, 2.5% pine oil	Bulatovic (2014)
LR19: 62% D30LR, 27% petroleum sulphonate, 9% kerosene, 2% pine oil	Bulatovic (2014)

Of these collectors, oleic acid and other tall oil fatty acids are consistently used in full-scale operations, although Bulatovic (2014) reported that the LR series mixtures, particularly LR19 which contained 27% petroleum sulphonate, resulted in improved spodumene recovery when compared to oleic acid alone. Amarante et al. (1999) found a mixture of 500 g/t oleic acid, 200g/t naphthenic acid and 3500 g/t of fuel oil to show better flotation performance and selectivity than oleic acid alone when tested on ore from northern Portugal. The majority of these collectors were tested under slightly alkaline pulp conditions (between pH 6.5 and 8.5), with the exception of sulphated, sulphonated and phosphorated fatty acid compounds which were tested in acidic pulp conditions (Norman and Gieseke, 1940).

At Kings Mountain operations 700 g/t of tall oil fatty acid was used to condition the ore at 55% solids before rougher-cleaner flotation to produce a concentrate assaying 6.34% Li_2O with 88.4% Li_2O recovery from a head grade of 1.4-1.5% Li_2O. At the Greenbushes operation in Western Australia, spodumene and tourmaline are floated together as a bulk concentrate from -250µm/+20 µm feed using a fatty acid collector and soda ash (Na_2CO_3) at pH 7-7.5 to produce a concentrate assaying 7.5% Li_2O with 0.4% Fe_2O_3 (Bale and May, 1989).

New collector mixtures have been tested (Xu et al. 2016), including mixtures of sodium oleate and dodecyl trimethyl ammonium chloride (DTAC) in different ratios with the objective to improve selective flotation of spodumene over other alumino-silicates such as feldspars. Tests were conducted on pure minerals (spodumene and feldspar) and ores from the Jiajika Lithium Mine in Sichuan Province, China. The authors found that a 9:1 optimal ratio of sodium oleate to DTAC, along with NaOH as a pH modifier and Na_2CO_3 as a feldspar depressant at pH 8-8.6 was most effective. It was possible to increase the spodumene concentrate grade by 0.31% Li_2O with no decrease in recovery. Further, the use of a collector mixture resulted in decreased reagent consumption compared to use of sodium oleate alone. The collector mixture was also less sensitive to a drop in pulp temperature.

Moon and Fuerstenau (2003) also investigated the effect of pulp temperature on sodium oleate adsorption on spodumene surfaces which was found to increase with increased temperatures when the critical oleate concentration was exceeded, and decreased with temperature (higher than 35°C) when the oleate concentrate was at starvation levels. This was possibly attributed to initial physical adsorption at low concentrations of collector.

Other collectors such as dodecylamine have been reported to produce better spodumene flotation results than oleic acid and other fatty acids (He et al. (2014). However, these studies were not conducted on whole ores or on associated silicate gangue minerals. While spodumene may be highly floatable using amine based collectors, it may be extremely difficult to achieve selective flotation over other silicates in real ore systems.

Tantalum Recovery. Tantalum can be a valuable by-product in spodumene ore if the head assay is high enough. Typically tantalum, which is found Ta-Nb oxide minerals, is recovered by gravity separation (Bale and May, 1989). Alternatively, magnetic separation can also be used to recover some tantalum oxide minerals.

Surface Chemistry Considerations
Collector Adsorption. The most significant study conducted on spodumene surface chemistry which relates to flotation was conducted by Moon and Fuerstenau (2003). The authors investigated the relationship between anisotropic crystallographic surface properties and oleate collector adsorption. It was found that oleate was chemisorbed onto aluminum sites at the spodumene surface. Moreover, contact angle measurements were higher on the {110} cleavage plane compared to the {001} crystal plane, indicating that there was preferential collector adsorption on {110} plane. This was credited to the fact that surface Al site on {110} plane has 2 unsatisfied coordinations ideal for oleate ion adsorption.

The implication of differential collector adsorption on different planes of the spodumene crystal structure has been identified recently by Xu et al. (2016) who recommended that comminution should be designed to promote the production of {110} cleavage planes for improved flotation. In this study, the flotation behavior and adsorption of sodium oleate was investigated on different size fractions. Of the size fractions tested, spodumene particles between 38µm and 45µm had the most {110} edges and also demonstrated the best floatability. Finer spodumene particles (<38µm) had more {001} basal planes (only one broken Al bond compared to 2 broken Al bonds on the {110} planes) and demonstrated much poorer flotation behavior. These findings are similar to those from earlier work conducted by Gasalia et al. (1987) to study the effect of impact and friction milling on physicochemical properties of spodumene. IR spectroscopy showed AlO_6 vibrations on the spodumene surface at frequencies of 916 cm^{-1}, 860cm^{-1}, 630cm^{-1} and 590 cm^{-1}. After shorter grinding times the observed absorbance increased slightly, but after long grind times the bands disappeared or decreased, likely corresponding to a reduction in {110} planes and an increase in {001} planes.

The pH of maximum sodium oleate adsorption was proven to be around pH 8 by Moon and Fuerstenau (2003) through Fourier Transform Infrared spectroscopy studies that showed adsorption at aluminium sites at this pH were strong and irreversible after washing. Further investigation by Yu et al. (2015) found that pH 8 not only corresponded to maximum flotation, but also to the formation of ionic and molecular complexes of oleic acid, suggesting that hydrocarbon chain associated may be partially responsible for good flotation at this pH. The association of the ionic and molecular forms of the reagent resulted in an increase strength of the bond between the COO^- group and the aluminum sites at the mineral surface.

Isoelectric Point. Zeta potential measurements conducted on a pure spodumene sample from Kings Mountain, NC by Moon and Fuerstenau (2003) identified the isoelectric point to be 2.3, similar to other silicate minerals. Torres Sanchez et al. (1989) conducted point of zero charge (pzc) measurements by titration on spodumene samples from the San Luis province in Argentina after grinding the pure mineral samples for 0 minutes, 5 minutes, 20 minutes and 50 minutes. It was found that the pzc increased with increasing grind time, likely in part due to increased formation of aluminium oxide at the mineral surface.

Effect of Ions on Spodumene Flotation. Dissolved ions are known to have an effect on flotation of minerals with fatty acid collectors (Nanthakumar et al, 2009). Most recently, the effect of calcium activating ions on the flotation of spodumene was investigated (Yu et al., 2014). Under slightly alkaline pulp conditions, characteristic of those in spodumene flotation circuits with fatty acids, the dominant calcium species were found to be $Ca(OH)^+$ and $Ca(OH)_2$. This corresponds to the maximum floatability of spodumene, and it was suggested that the precipitation of calcium hydroxide on the surface of spodumene was responsible for this activating effect. Wang and Yu

(2007) found that both Ca^{2+} and Fe^{3+} in the flotation pulp resulted in spodumene activation. Activation with Ca^{2+} took place at pH 11.7, likely due to the precipitation of calcium hydroxide on spodumene surfaces. Fe^{3+} showed a stronger activating effect than Ca^{2+}, which took place in the pH range between 6 and 9. Moon and Fuerstenau (2003) observed similar phenomena, with ferric impurities leading to activation of spodumene at pH 4 when floated with sodium oleate. These studies neglect to highlight that calcium hydroxide and ferric species are likely to precipitate on the surface of other silicate gangue minerals as well as spodumene surfaces, which can be the cause of concentrate grade dilution. Therefore process water chemistry is likely to have a significant effect on overall flotation performance of spodumene, an area that warrants further study.

Magnetic Separation

Magnetic separation is frequently used to reject iron bearing minerals so that the spodumene concentrate is suitable for use in ceramics and glass applications. Magnetic separation can be conducted at various intensities on different streams in the circuit. While it is most common to perform magnetic separation in the final spodumene concentrate, it can also be carried out on the flotation feed. Magnetic separation on the flotation feed may be beneficial it the objective is to remove large quantities of amphibole (can be separated at a magnetic intensity of ~10000 Gauss), which would otherwise report to the flotation concentrate. The use of different types of magnetic separation have been reported for this application including HGMS (high gradient magnetic separation) and WHIMS (wet high intensity magnetic separation) (Bale and May, 1989; Jirestig and Forssberg, 1994).

Jirestig and Forssberg (1994) conducted magnetic separation testing on spodumene flotation and concluded that effectiveness of magnetic separation is related to particle dispersion in the feed. Recovery to the magnetic fraction improved by 10% when pulp pH was dropped to pH 2 using sulphuric acid for better particle dispersion. It was hypothesized that residual collector can be responsible for flocc formation in the spodumene concentrate. Dropping the pulp breaks the floccs by precipitating oleic acid. By conditioning the pulp at pH prior to magnetic separation the authors were able to improve Li_2O grade of the concentrate by 0.15% with a 0.35% in Fe_2O_3 grade. Lithium losses to magnetic product were reduced by 1.13%.

Roasting

Spodumene can exist in α, β, or γ forms. In order to extract lithium from spodumene, the crystal structure of the mineral must be converted from its monoclinic α-form (as mined and concentrated) into a tetragonal β-form. This is accomplished through the addition of heat, most commonly in conventional resistance heated furnaces at a temperature of $1050^{o}C$ (Bale and May, 1989; Peltosaari, 2015). Once spodumene is in beta β-form, then the lithium in the crystal structure can be replaced with sodium or hydrogen ions under high temperature or high pressure conditions to eventually (by means of lithium sulphate) produce a final product of lithium carbonate or lithium hydroxide. The details of this process are not covered in this review.

During the heating process particles first undergo a size reduction and then expansion followed by breaking apart, resulting in a reduced P_{80} and specific gravity after roasting. A study of spodumene from Greenbushes transformation by conventional heating (muffle furnace) showed that structural changes were observed in the spodumene crystal after heating at $950^{o}C$ for 30 minutes. After heating longer than 10 minutes at $1100^{o}C$, complete transformation of α to β and γ spodumene occurred. This corresponded with volumetric expansion and a concentrate colour change from beige to white (Salakjani et al., 2016). The roasting process is complicated by a large feed size distribution (as can be the case when both DMS and flotation concentrates are produced) and by impurities in the concentrate. In particular, iron bearing silicate minerals can be quite problematic as they tend to soften at high temperature and cause agglomeration of spodumene particles during the roasting process.

Novel research in this area includes investigation into the use of microwave heating as an alternative to conventional heating. Initial results from work conducted by Peltosaari et al. (2015) showed that for full conversion of α-spodumene to β-spodumene, heating time was reduced significantly when using a microwave compared to conventional heating. The potential energy and cost savings associated with microwave heating are not clear at this time.

SUMMARY AND CONCLUSIONS

The current beneficiation methods used to upgrade spodumene from hard rock deposits are quite complex and few major improvements to the process have been made in the past few decades. Future research should focus on the development of effective comminution circuits to reduce energy consumption and maximize the generation of {110} cleavage planes on spodumene grains to improve flotation performance and lithium recovery. Further reagent mixtures that have demonstrated improvements in selectivity over other alumino-silicate minerals should be investigated further and tested at the pilot scale or in full-scale operating plant trials.

Roasting is one of the most energy intensive steps among all the beneficiation processes until operations. Research and development in this area, either through examination of alternative heating methods or through the development of downstream processes that allow for the elimination of roasting altogether, is imperative for the economic development of additional hard-rock lithium deposits globally.

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