

Effect of waste rock dilution on spodumene flotation

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Highlights

- The effects of waste rock dilution on spodumene ore flotation were investigated using a spodumene ore with 12% dilution
- Mg-bearing biotite and amphiboles are the main gangue minerals deteriorating quality and yield of concentrate
- MgO recovery behaves the same way as Li₂O recovery in the spodumene flotation
- Different reagents and varying water quality were used in flotation tests to study their effects on grade and recovery of diluted spodumene ore

Abstract

The effect of waste rock minerals introduced by dilution on the flotation of spodumene was investigated. The objectives of this work were to investigate how flotation yield and grades deteriorate mainly by Mg-bearing biotite and amphiboles that are introduced to the system by waste rock dilution and find the possible ways to improve the flotation performance regarding these Mg-bearing minerals.

Laboratory flotation tests were conducted with modifications to the standard procedure and new conditions. Analytical methods used in this work include mineralogical tests like electron probe micro-analyzer (EPMA) to find out accurate elemental assays for the minerals in the deposit, especially biotite. X-ray fluorescence (XRF) and atomic absorption spectroscopy (AAS) to analyze flotation products contents. Mineral liberation analysis (MLA) for liberation, associations, Mg-distribution and modal mineralogy. Information about mineral recoveries in different flotation stages was obtained from element to mineral conversion calculations with HSC Chemistry software.

The target grade and recovery of Li₂O for the Rapasaari ore were established on 4.5 % and 84.18 % (as a previous standard test). The use of Na₂CO₃ and starch modifiers gave promising results slightly improving the recoveries to 85.29 % and 85.11 % respectively while reaching almost 4.5 % grade in final concentrate.

Mineral liberation analysis (MLA) showed that biotite contains most of the Mg (80-90 %), other minerals are amphiboles (mainly edenite and hornblende) and in less extent chlorite and clays. Biotite and amphiboles end up in the final concentrate mostly fully liberated while apatite is mostly coarse mixed grains. Mg-bearing minerals float into the concentrate because of similar surface properties with spodumene. Those similar properties may be due to chemically active Al-O sites that form on the mineral surfaces when the mineral breaks through its cleavage planes during comminution. Al-O sites act as collector attachment spots in fatty acid flotation and compete for collector adsorption.

Key words: Dilution, spodumene, flotation, waste rock, Mg-bearing minerals

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1. Introduction

Most of the lithium production from hard rock deposits comes from spodumene ($\text{LiAlSi}_2\text{O}_6$) and petalite ($\text{LiAlSi}_4\text{O}_{10}$) and less from lepidolite ($\text{K}(\text{Li},\text{Al})_3(\text{Al},\text{Si},\text{Rb})_4\text{O}_{10}(\text{F},\text{OH})_2$) and amblygonite ($\text{Li},\text{Na})\text{AlPO}_4(\text{F},\text{OH})$). They all have different chemistry when it comes to their enrichment processes (Bulatovic 2015, Swain 2016). These minerals are mined using conventional techniques and processed typically through circuits including dense media separation, magnetic separation and flotation among others, depending on deposit to produce a concentrate that is often, after high temperature pretreatment processed into high purity lithium carbonate of more than 99.5 % (Staiger & Rödel 2017).

Spodumene is a type of monoclinic pyroxene mineral with a single-chain structure and chemical formula of $\text{LiAlSi}_2\text{O}_6$ that is most commonly found in granitic pegmatite rocks (Moon, K. S., Fuerstenau 2003). Typical minerals associated with spodumene include albite ($\text{NaAlSi}_3\text{O}_8$), quartz (SiO_2), petalite ($\text{LiAlSi}_4\text{O}_{10}$), eucryptite (LiAlSiO_4), beryl ($\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$) and different kinds of mica like biotite ($\text{K}(\text{Mg},\text{Fe})_3(\text{AlSi}_3\text{O}_{10})(\text{F},\text{OH})_2$), muscovite ($\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{F},\text{OH})_2$) and lepidolite ($\text{K}(\text{Li},\text{Al})_3(\text{Al},\text{Si},\text{Rb})_4\text{O}_{10}(\text{F},\text{OH})_2$) (Jie et. al. 2017). Although pegmatites are not particularly unusual, lithium-bearing ones can be considered relatively rare (Evans 2014, Brown et al. 2016).

Typical gangue minerals of spodumene and lithium ores are oxides and silicates and they are the most diverse group of minerals when it comes to flotation. Their flotation can be conducted with many different collectors depending on mineral surface properties like isoelectric point and the so-called active sites on the mineral surface.

Achieving selective separation of minerals in a flotation system requires that there is a way to make some mineral particles hydrophobic and others hydrophilic. It is well known that selective separation among oxide, silicate and hydroxide groups can be quite difficult due to their similar surface properties after comminution process (Hu et al. 2003). These similar surfaces originate from the minerals' crystal structures and elements in those structures. It has been shown that the active site for oleate collector attachment in spodumene and other aluminium-containing silicates like feldspar, muscovite, amphiboles and biotite is in-fact the broken aluminium-oxygen bond and secondarily the exposed metal cation site in the crystal structure (Rai et al. 2011).

The first spodumene rock deposit in Northern Europe will enter in operation in 2021. Pilot and laboratory scale tests done in recent years have given promising metallurgical results to produce lithium carbonate but there is room for optimization. Past research with Keliber's ore showed that biotite and amphiboles are the main gangue minerals outside of silicates that end up floating into the final concentrate with spodumene, which is troublesome because MgO impurities in the concentrate can cause problems regarding the later metallurgical processes in the production chain.

1.2 Waste rock dilution

Waste rock dilution can be defined as the contamination of ore with lower grade waste rock material. Waste rocks can contain gangue minerals outside of the actual planned ore body, which can affect the production process in several negative ways, or it can consist of low-grade ore that did not make up the cut-off grade. Dilution is considered as one of the most important factors affecting the economy of mines (Ebrahimi 2013). Some degree of dilution is always expected to happen, and a mineral processing circuit needs to be built and optimized having that in mind. Possible optimizations include additions of pre-concentration unit operations like magnetic separator to minimize the adverse effects of some of the gangue minerals or for example introducing extra chemicals to the flotation process to depress gangue minerals from the waste rocks. This dilution can be calculated with the following equation:

$$D(\%) = \frac{Q_w}{Q_f} * 100 = \frac{Q_w}{Q_o} * 100$$

Where D (%) is the dilution in %, Q_w is the amount of waste rock, Q_f is the amount of mill feed and Q_o is the amount of ore.

Dilution is usually divided into planned and unplanned dilution. Planned dilution also referred to as primary or internal dilution is contamination of ore by low-grade material from within the ore block and unplanned dilution, also known as secondary or external dilution, is contamination of ore outside the ore block. Both of these dilute the mill feed and cause several issues and expenses during the project (Jang et al. 2015).

The current flotation circuit shows grade and recovery deterioration when waste rock dilution is introduced to the system. Waste rocks from different deposits contain different minerals than the ore itself and seem to float with spodumene or by other means and concentrate into the last cleaner stage, which negatively affects the concentrate quality. Especially magnesium containing minerals like biotite and amphiboles are prime suspects to be the main cause of negative results as they have shown good floatability in the same conditions as spodumene

2. Materials and methods

Several mineralogical and analytical methods were applied in conjunction with batch flotation tests in laboratory scale.

2.2 Materials

Rapasaari ore from the largest Keliber's ore deposit was used in this work. A blended sample of 12 kg with 12 % diluted ore was prepared to use 1 kg of ore for each flotation batch test. The preparation of the blending included; first, a representative Rapasaari ore crushed to -3.35 mm and split to obtain 10.56 kg. Waste rock (1.44 kg) crushed to -3.35 mm and combined with Rapasaari ore and homogenized, then divided into 1 kg of blended ore samples using laboratory scale riffle splitter and rotary cone sample divider to get an even and random division.

Main flotation reagents that were used in the tests were collector PRIFAC 8944-LQ-(GD) rapeseed fatty acid (Croda) later denoted as RSFA, emulsifier BEROL 050 (Akzo Nobel) and on some tests collector ATRAC 922 (Akzo Nobel).

PRIFAC is an oleic acid rich fatty acid mixture consisting mostly of oleic acid ($C_{18}H_{34}O_2$) (55-65%) and linoleic acid ($C_{18}H_{32}O_2$) (18-24%) that are also the main working components providing the collector effect. BEROL 050 emulsifier is added to ease the mixing of fatty acid collectors in water and it consists of polyether alcohols of formula $R-O-(CH_2CH_2-O)_n-H$ where R is a C-12 through C-16 alkyl group and n equals 1 through 6. Atrac 922 is a flotation chemical that's main components are N-[2-hydroxy-3-(C12-16-alkyloxy)propyl]-N-methyl glycinate (40-50%) and branched and linear ethoxylated alcohols C12-13 (20-25%), which acts as a premade collector / emulsifier mixture, where the first component acts as a collector and the ethoxylated alcohols as emulsifiers

2.3 Modal mineralogy

The average qualitative and quantitative mineralogy of Rapasaari ore and waste rock was determined by MLA as is shown in Table 1

Table 1 Rapasaari ore and waste rock modal mineralogy determined by MLA

Mineral	Average ore Wt%	Waste rock Wt%
Quartz	27.21	23.53
Plagioclase	33.37	30.03
Microcline	16.76	1.56
Spodumene	13.19	0.02
Cookeite	0.28	0.02
Muscovite	7.61	7.69

Biotite	0.05	24.20
Chlorite	0.08	2.05
Clay	0.26	1.21
Montmorillonite	0.02	0.55
Garnet	0.31	0.01
Tourmaline	0.21	2.52
Epidote	0.00	1.76
Titanite	0.00	0.45
Forsterite	0.00	0.07
Amphibole	0.00	1.99
Zircon	0.00	0.01
Apatite	0.21	0.65
Sicklerite	0.19	0.00
Calcite	0.03	0.46
Pyrrhotite	0.00	0.68
Pyrite	0.03	0.04
Arsenopyrite	0.01	0.09
Process Metal	0.04	0.02
Unknown	0.13	0.36
Total	100.00	100.00
Nr of measured particles	20258	20186

2.4 Flotation tests

A series of batch flotation tests were performed in GTK Mintec Outokumpu investigating the effects of different reagents and water quality for improvement of the results from the current standard flotation procedure. The set up conditions used in this work are summarized in Table 2.

Table 2 Flotation test plan, conditions and objective

Test no.	Description	Objective
1	Standard Test, same as previous Rapasaari reference test (Test 11). Filtrate waters from Rougher and Cleaning flotation are collected for the next test.	To see how different flotation machine and operator affects the results compared to reference test Rapasaari Test 11
2	Same as Test 1, but lowered collector dosages and tailings waters from Test 1 are used in spodumene flotation. Filtrate waters are collected again.	To study the effects of recirculated waters and ion concentrations on floatabilities of minerals in spodumene flotation.
3	Same as Test 1, but recirculated water from GTK pilot pond is used in preflotation and spodumene flotation.	To study the effects of waters containing elevated amounts of ions in preflotation and spodumene flotation.
4	Same as Test 1, but Na ₂ CO ₃ is used as a modifier in spodumene flotation.	To study the effects of Na ₂ CO ₃ as a modifier.
5	Same as Test 2, but tailings waters from Test 2 are used in spodumene flotation.	To study the effects of recirculated waters and even higher ion concentrations on floatabilities of minerals in spodumene flotation.
6	Same as Test 1, but starch is used as a modifier in spodumene flotation.	To study the effects of starch as a modifier.
7	Same as Test 1, but Atrac922 from Akzo is used as collector chemical in spodumene flotation without emulgator.	To study the effects of different collector.
8	Preflotation test with two cleaning stages and increased chemical dosages.	To study the possibility to increase gangue mineral recovery in preflotation and recover spodumene lost in prefloated concentrate
9	Same as Test 7, but adjusted the amount of collector based on analysis from Test 7.	To study the effects of different collector.

The standard procedure (Rapasaari Test 11) was used as a reference. In order to obtain p80 of 130 µm, first, the 1 kg of ore was ground for 20 min at 53 % solids in an iron rod mill (22 cm length and 18.8 cm diameter)

with 8 kg of rods of 20.3 cm in length and three diameter sizes 2.5 cm, 2.0 cm and 1.5 cm. The ground sample was sieved (150 μm) and the oversize sample (+150 μm) was re-ground for 8 minutes (in the same mill).

Desliming was conducted by elutriation in 4 liters Outokumpu's cylindrical flotation cell using 650 rpm rotor speed and 0.18 l/min water flow. Water was fed into the cell from the bottom of the cell through the rotor water outlet. Correct water flow was calculated using the Stoke's Law, the target fineness of slimes fineness (p80 11 μm) and the diameter of the flotation cell. The desliming time was set in 35 minutes.

The slurry settled overnight to eliminate the excess water by decantation and obtain 4 liters of pulp with 60 % solids. The pH of conditioning for preflotation was set to be above 10.5 in a 4 liters GTK flotation cell with 1800 rpm, 500 g/t of NaOH for 15 minutes, the collector rapeseed fatty acid (RSFA 120 g/t) and emulsifier Berol 050 (30 g/t) were conditioned for 5 minutes each.

In preflotation, naturally and easily floating gangue minerals like apatite and calcite were floated. Addition of fatty acid lowers the pH, but more NaOH was added if necessary. The preflotation was done with 3 l/min airflow, 1800 rpm and 30% of solids for 4 minutes with an automatic scraping of froth.

The tailings of preflotation were treated by wet low intensity magnetic separation using a SALA equipment with an operating intensity of 0.07 Tesla ($\text{Kg/s}^2\text{A}$). The objective was to remove the ferromagnetic minerals (magnetite, pyrrhotite, etc.) and process iron. Magnetic material was filtrated, dried and bagged for analysis and non-magnetics were left to settle for excess water removal by decantation to fit in 2.5 liter flotation cell and 60 % solids. This pulp was conditioned adjusting the pH to 7.5 with acid titration by sulphuric acid (H_2SO_4) and 1500 rpm. After pH adjustment, the collector rapeseed fatty acid (1300 g/t) and emulsifier (325 g/t Berol 050) were added and conditioned for 5 minutes each.

Rougher flotation time was 7 minutes with 2 l/min air, 30 % solids and automatic scraping. After the rougher flotation, the concentrate was cleaned seven times. Collector and emulsifier are added in first three cleaning stages (Cleaning 1: 400 g/t RSFA/100 g/t Berol, Cleaning 2: 300 g/t RSFA/75 g/t Berol, Cleaning 3: 200 g/t RSFA/50 g/t Berol) with conditioning times of 3 minutes each. First cleaning was done in the same 2.5 liter cell with same air and rotor rpm, cleanings 2-7 were done in 1.5 liter cell with 1.5 l/min air, 1100 rotor rpm and manual scraping of froth. Flotation times for cleanings were as follows: C1 and C2: 6 minutes, C3: 5.5 minutes, C4: 5 minutes, C5: 4.5 minutes, C6: 4 minutes and C7: 3.5 minutes.

Filtrated water samples from rougher tailing and cleaning waters (from tailing and concentrates from couple of tests) were collected to be reused. The objective was to study the effects of different metal ions and chemicals that are introduced into the process water when recycled water is used and the effects of different modifier reagents that have proven to be useful in other research work and mine operation regarding spodumene beneficiation.

A preconcentrate cleaning test (Test 8) was done by increasing the dosage of reagents in the preflotation stage from 120 g/t to 200 g/t of collector and from 30 g/t to 50 g/t of emulsifier and then running two cleaning flotations on the concentrate from the preflotation. Cleaning flotations were done with no chemical additions or pH adjustments, but pH naturally decreased to around 9 in first cleaning and to around 8 in the second cleaning because of water added to adjust the flotation pulp level during the test.

2.5 *Analytical methods*

2.5.1 **Optical microscope**

Polished sections of the final concentrate, average ore and waste rocks of different Keliber's deposits were prepared and analyzed with optical microscope to have initial lower resolution look at the samples and to pinpoint the locations of different minerals for EPMA analysis.

2.5.2 Mineral Liberation Analyzer (MLA)

Seven samples of feed and flotation products were cast into epoxy in thin section mould and analysed using the MLA equipment FEI Quanta 650F FE-SEM scanning electron microscope with acceleration voltage of 25 kV and emission current of ~207 μ A. Backscattered electrons were analyzed with 100x magnification for +125 μ m fraction and with 400x magnification for -32 μ m fraction. The measurement program was XBSE_STD.

Thin sections were produced from Rapasaari Feed 12 % Dilution bulk, Rapasaari Feed 12 % Dilution +125 μ m, Rapasaari Feed 12 % Dilution 32-125 μ m, Rapasaari Feed 12 % Dilution -32 μ m, Rapasaari AT Test 4 PR, Rapasaari AT Test 4 CC7 and Rapakeli Test 11 CC7.

The number of particles measured was 60 000 for every sample, except for Rapasaari Feed 12% Dilution +125 μ m since it only contained about 20 000 particles.

Modal mineralogy, spodumene, apatite and biotite liberation, Mg distribution, Li mineral, biotite, amphibole and apatite mineral associations were determined with the MLA from all samples before mentioned.

2.5.3 Electron probe micro-analyzer (EPMA)

The elemental composition of minerals was determined with EPMA model JEOL JXA-8200 SuperProbe WD/ED Combined Microanalyzer while used acceleration voltage was 15 kV, probe current 15 nA and probe diameter 5-10 μ m depending on mineral grain size. Measurement points were chosen in the sample especially to analyze the Mg-bearing gangue mineral compositions that were of interest i.e. biotite and amphiboles. Results were used in element to mineral conversion calculations.

2.5.4 Element to mineral conversions (EMC)

EMC calculations were performed with HSC Chemistry version 9.2.2 from Outotec (Geo module). The modal calculations use the analyzed XRF chemical assays and qualitative mineralogy.

The elemental compositions from EPMA results were input in HSC Chemistry for the minerals that were analyzed, and stoichiometric compositions from the program's mineral database were used for common minerals.

3. Results and Discussion

3.1 Biotite composition

The Mg-bearing minerals were of special interest in this work of which biotite proved to be the most relevant to focus since the MLA analysis showed that it contains around 80-90 % of the magnesium in the minerals (Table 5). Biotite elemental composition was calculated from EPMA analysis and it is presented in Table 3 .

Table 3. Biotite composition calculated from EPMA analyses

Element %	Si	Ti	Al	Fe	Mn	Mg	Ca	Na	K	O
Biotite	17.48	1.32	10.10	13.64	0.21	6.92	0.01	0.01	7.32	42.99

The spodumene ore itself doesn't contain Mg-bearing minerals (biotite and amphiboles) but they are introduced into the system when the ore is diluted with waste rock, which is almost impossible to prevent in an economically feasible way with current mining methods because of the uneven distribution and shape of the ore body in the deposit.

Mg, Al, K and Si are the major elements in the composition of Biotite. Mg content is 6.92% and assumed to have a negative effect on the flotation. Previous studies showed flotation results with waste rock diluted ore containing biotite and amphiboles build up in the final concentrate and reduce concentrate grade and recovery in addition to increasing the chemical consumption (Salvador 2017). Biotite also causes problems in

the next stages of the lithium carbonate production chain by promoting partial melting of the concentrate when it is processed in high temperature (1050 °C to transform alpha spodumene into digestible beta spodumene). Formation of the partial melt can cause agglomeration during the lithium digestion procedure, which lowers the lithium recovery and makes the process more difficult to operate (Tanskanen 2018).

3.2 Li_2O grade – recovery

Figure 1 shows the profiles of Li_2O grade vs recovery from tests carried out under different conditions. The referential standard test (test 11) has 87.81% recovery and 4.47 % grade and the same conditions were used for the Test 1 showing lower recovery (83.43%) and higher grade (4.7%). The target Li_2O grade for Rapasaari ore concentrate was determined to be 4.5 % in the pre-feasibility study published in 2016 and achieved in this test.

Tests 4 and 6 (Na_2CO_3 and starch modifiers) show the higher Li_2O grades of 4.9 and 4.75 % and recoveries of 82 and 83.5 % respectively. The ore showed higher kinetic of flotation requiring less time of flotation to get the targeted grade of 4.5% and recoveries higher than 85% with both conditions. Those grades and recoveries could be found in the concentrate of fifth cleaner (CC5) for Test 4 and in cleaner six (CC6) for Test 6. More tests with these modifiers will be required in the future in order to improve the conditioning and dosage.

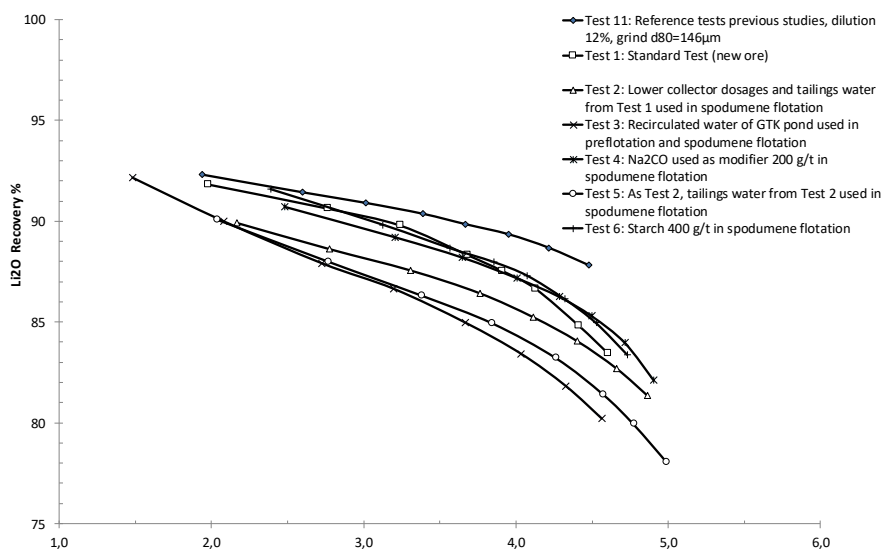


Figure 1. Grade-recovery curves of flotation tests with Rapasaari ore and various conditions

Water samples were taken during all the flotation tests showing clearly that increasing amounts of metal ions in the process water decrease the spodumene recoveries and overall flotation results.

Tests 2 and 5 were done with recirculated tailing waters and show the build-up of metal ions in the water analysis with consecutive uses of the same water. These tests also showed decreasing Li recoveries in the final concentrate proportional to the increment of metal ions and more recycled water (test 5 less recovery than test 2), as minerals dissolve in the water and water species (metal ions) undergo various reactions (adsorption, complexation, precipitation) that affect interfacial reactions.

Test 3 was done with GTK pilot pond water (containing higher amounts of various metal ions Ca, Na and Mg) gave the lower recovery and grade. Other species in water such as decomposition products of remaining reagents in the water or complexation of various components and differences in reagent dosages could also affect these results.

A different collector (Atrac922 from Akzo) was tested in Test 7 and 9 for spodumene flotation without emulgator. In addition, preconcentrate cleaning (Test 8) was attempted to improve the flotation of spodumene. The results were not satisfactory (not shown here) and more research is recommended.

3.3 Mineral Liberation

Mineral liberation for spodumene, biotite and apatite were measured for seven samples (bulk and sized feed and products) as is shown in Figure 2 to 4. Liberations were determined as mineral grains (wt-%) proportions. The x-axis shows the minimum mineral content that is being observed for the grains and the y-axis shows the number of grains in percentage that fulfil that proportion.

Results for spodumene liberation show that spodumene is well liberated having around 80-90 % of grains as pure grains and around 95 % of grains being 90-95 % spodumene, which shows that grinding times were sufficient regarding spodumene flotation (Figure 2).

The concentrate shows 80 % of biotite grains (Figure 3) are pure grains and around 90 % are minimum 75-80 % biotite. Both concentrate samples and the 32-125 µm fraction grinding product sample are about the same. Biotite preconcentrate liberation curve acts the same way with the before mentioned samples but has overall higher grain purity of around 90 % of grains being pure and 95 % being 90-95 % purity. In -32 µm fraction around 97 % are pure grains. In +125 µm fraction, around 60 % of grains are pure, around 80 % being minimum 55-60 % biotite and 90 % is only 25-30 % minimum purity.

For apatite liberation (Figure 4) in sample Rapasaari Test 4 CC7, around 40 % of apatite is fully liberated and around 60 % of grains contain minimum 90 % of apatite. Apatite curves are bit more all over the place. In test 4 sample, 90-95 % purity is still attained in 60 % of grains while in the reference test (Test 11) 60 % of grains have only a minimum of 20-25 % purity. For the coarse +125 µm grinding product sample, around 60 % of grains are pure and 80% contain minimum of 30-35 % apatite. The 32-125 µm mid fraction has around 70 % fully liberated and 80 % still having minimum of 85-90 % apatite. In the bulk grinding product and preconcentrate samples 80 % of apatite is pure and in the -32 µm fraction it is almost fully liberated.

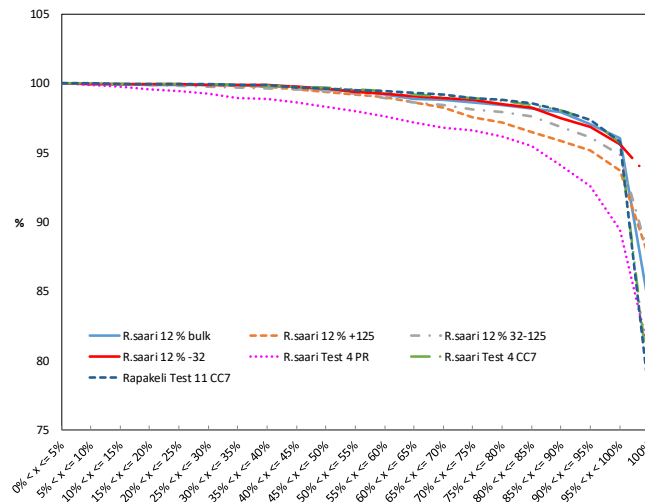


Figure 2. Spodumene liberation

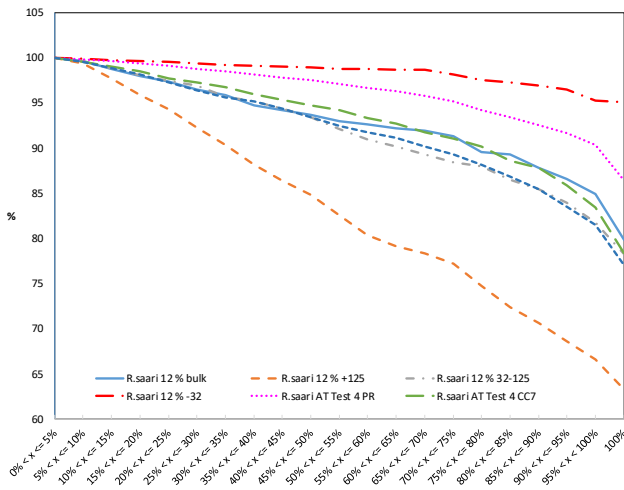


Figure 3. Biotite liberation

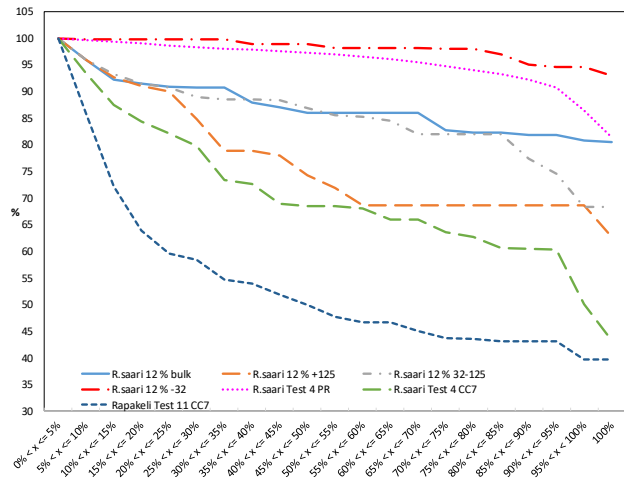


Figure 4. Apatite liberation

3.4 MgO grade – recovery

MLA analysis regarding magnesium distribution showed that biotite contains around 80-90 % of the magnesium in the minerals, which means that looking at the MgO grades and recoveries can give a good picture of how the flotation of Li_2O is affected by biotite and other Mg-bearing minerals.

Flotation results show that MgO grade-recovery curve (Figure 5) is comparable with Li_2O grade-recovery in the spodumene, indicating that biotite and amphiboles have similar surface properties with spodumene.

In general, the recovery and grades of MgO were higher than 50% and 1.3% respectively. When using starch modifier (test 6) recovery and grade of MgO are the highest in all stages reaching 58% and 1.34% in the 6th cleaner when Li_2O reach the target grade 4.5%. The elevated metal ion content in the process waters in tests 2, 3 and 5 might affect Mg-bearing minerals recovery and possibly depress them slightly. However, spodumene recoveries were also decreased in the same tests (2, 3 and 5) which suggests even further related flotation behaviour.

MgO is recovered much more into slimes and preconcentrate than Li_2O so these process stages are probably worthwhile to investigate for possible improvements for selectivity. Same flotation reagents are used in the current preflotation recipe as in the spodumene flotation, which might be the reason for some of the spodumene losses in the preconcentrate even though the pH is very different.

The average distribution of MgO and Li recovery in the flotation test products can be seen in Table 4 and Table 5. Average recovery values from tests were calculated for flotation products and as it is evident that around 9 % of MgO is recovered into slimes, 11 % into preconcentrate (PR), 50 % into final concentrate (CC7) and rest are evenly distributed into tailings. This recovery distribution follows the same pattern with Li except for the slimes and preconcentrate recovery where more MgO is recovered. Still, the majority of the MgO is building up into the final concentrate.

Table 4. Average distribution of Li recovery between flotation test products (PR=Pre-concentrate M=Magnetic fraction of tailings, RTails= Rougher Tailings, CT1 to CT7= Cleaner Tailing 1 to 7, CC7= Spodumene concentrate)

	Slime1	PR	M	RTails	CT1	CT2	CT3	CT4	CT5	CT6	CC7	CT7
Li_2O	3.81	1.87	0.46	2.82	1.67	1.30	1.15	1.17	1.26	1.46	81.43	1.61

Table 5 Average distribution of MgO recovery between flotation test products

	Slime1	PR	M	RTails	CT1	CT2	CT3	CT4	CT5	CT6	CC7	CT7
MgO	9.09	11.04	0.76	4.67	4.85	3.63	3.03	2.82	2.95	3.22	50.52	3.43

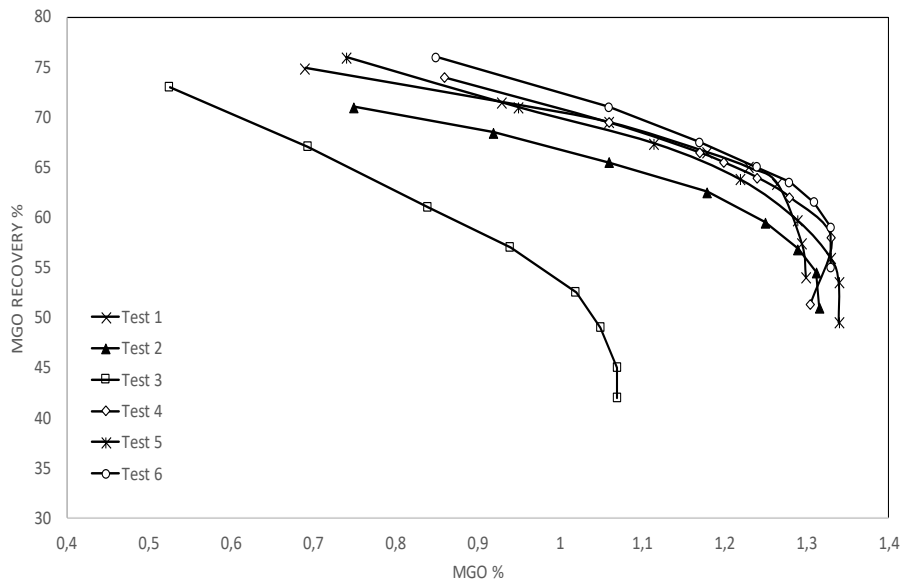


Figure 5. MgO grade - recovery curve from rougher concentrate to final concentrate

The interest in this work are the magnesium-bearing minerals thus the Mg-distribution between different minerals was determined based on the MLA results. Biotite contains the majority of the magnesium in all the samples, but other noteworthy minerals include amphibole and chlorite. The Mg-content of amphiboles, chlorite and clay minerals was determined from semi-quantitative EDS-spectra gained from the scanning electron microscope analyses. Other minerals were determined by stoichiometric Mg-content. Figure 6 shows the Mg-distribution between different minerals.

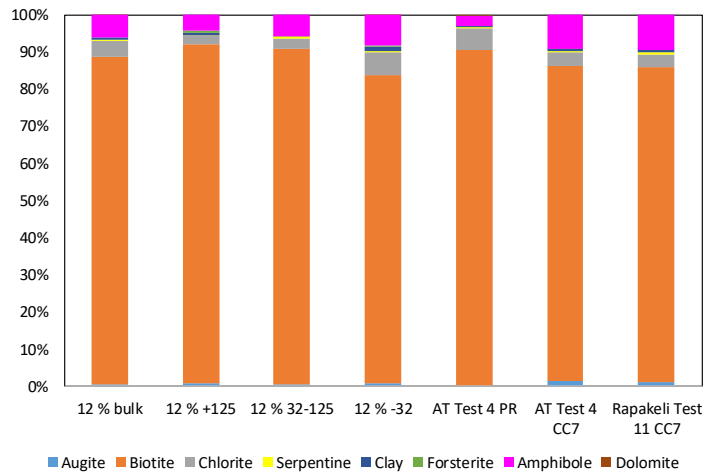


Figure 6. Mg distribution between minerals in different samples of Rapasaari ore.

3.5 Mineral association

Mineral associations for lithium minerals, biotite, amphibole and apatite were determined for six samples (Figure 7) to find out what minerals are floating into the concentrate.

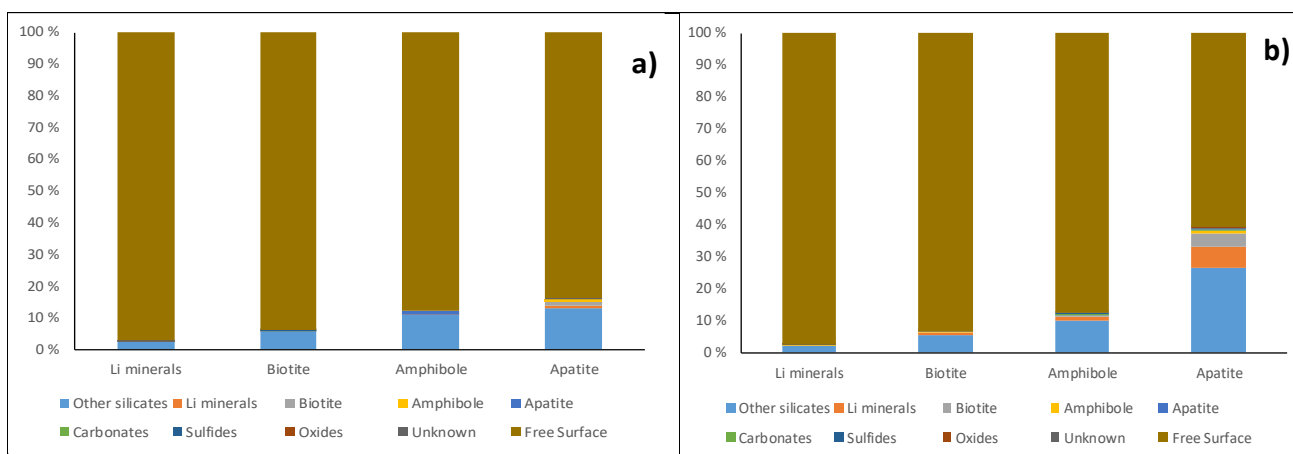
Li minerals are spodumene, cookeite, bityite and sicklerite. Other silicates are quartz, plagioclase, microcline, augite, muscovite, chlorite, serpentine, garnet, epidote, tourmaline, titanite, zircon and clay. Carbonates include calcite. Sulphides include pyrite, pyrrhotite, sphalerite, arsenopyrite and chalcopyrite. Oxides include columbite, rutile and ilmenite.

Overall, lithium minerals are almost totally liberated. Especially spodumene free surface is in great level on all the samples (~97%), even in +125 µm fraction. Cookeite and sicklerite are also well liberated having a free surface of 82-96% in all the samples except for the +125 µm fraction where the free surface is around 68% for cookeite and 75% for sicklerite. Main associations for cookeite are with quartz (8%) and spodumene (10.6%) and for sicklerite respectively apatite (16.8%) and less quartz (2.5%), plagioclase (2.1%) and microcline (2.3%). Bityite free surface is varying from 50-80% depending on fineness except for preconcentrate where it is well liberated (94.5%). Main associations overall include quartz (12-28%) depending on size fraction and on +125 µm fraction biotite (10.4%) and amphibole (7.4%).

Biotite is one of the main troublemaker minerals that are causing problems for the concentrate quality. In the grinding products, biotite is well liberated especially in the smaller particle fractions having 98% (-32 µm), 92% (32-125 µm) and 94% (bulk) free surface and 82% in +125 µm fraction. Main associations in the largest fraction include plagioclase (8.5%) and quartz (5.5%). In preconcentrate, biotite is fully liberated (97%). In the concentrate samples, biotite has around 93% free surface, which indicates that biotite is floating into the product because of its similar surface properties to spodumene and other floating minerals.

Amphiboles are the other Mg-bearing minerals that are of interest. Like biotite, they are floating in some amounts to the last flotation product and reducing the final concentrate quality. Overall, amphiboles are well liberated in all samples having 77-98% free surface depending on fraction size. Main associations include silicates like quartz (5.1%), plagioclase (9.1%) and muscovite (3%) in coarse fraction. In preconcentrate, amphiboles are almost fully liberated like biotite having 94% free surface and in the final concentrate also having around 87% free surface with small associations with before mentioned silicates.

Additionally, associations for apatite were determined. Apatite is the main P-containing mineral that is separated in the preconcentrate flotation. Of all the mineral categories that associations were determined in these MLAs, apatite has the greater associations. In bulk grinding product, apatite has around 84% free surface, but when looking at fractions, it has only 60% in +125 µm fraction and 71% in 32-125 µm fraction, while -32 µm fraction is almost fully liberated with 97% free surface. In preconcentrate, apatite is almost fully liberated with around 95% free surface but when looking at the final spodumene concentrate samples. Apatite that builds up into the spodumene concentrate is heavily associated with other minerals with around 60% free surface, which indicates that coarse mixed grains are the ones that end up in the final concentrate. Main associations of apatite in the concentrate samples include plagioclase (10-14%), quartz (6%), spodumene (4-8%) and biotite (4.5%).



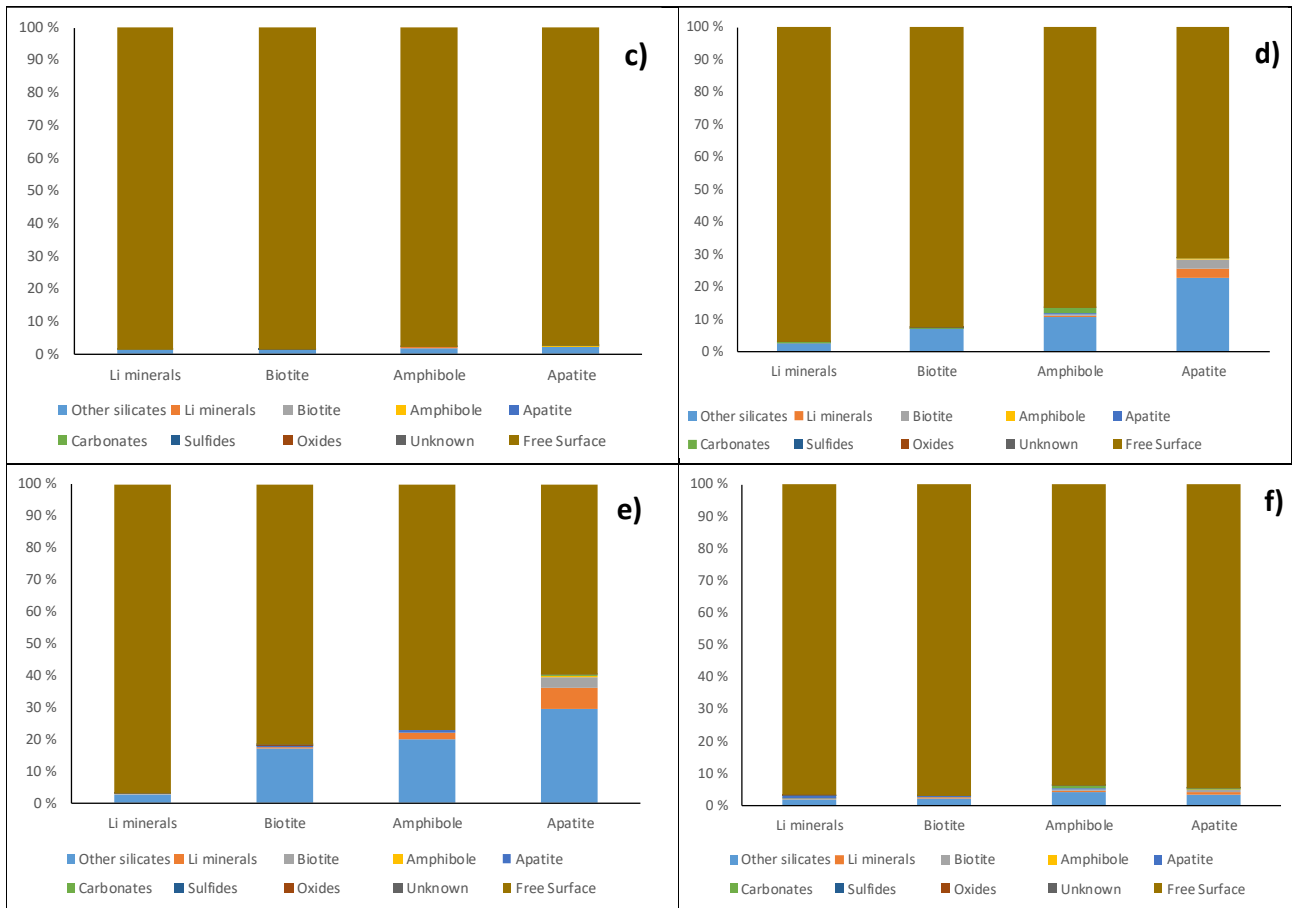


Figure 7. Lithium mineral, biotite, amphibole and apatite mineral associations in a) grinding product, Rapasaari Bulk 12% dilution b) in final concentrate (Test 4 = Na₂CO₃ modifier) c) in grinding product -32 μm fraction sample d) in grinding product 32-125 μm fraction sample e) in grinding product +125 μm fraction sample f) in preconcentrate (Test 4)

It is clear that most of the Mg-bearing minerals (biotite and amphiboles) are fully liberated particles floating into the spodumene concentrate and due to their similar surface properties cause a negative effect on concentrate quality. Those tend most likely to float into the concentrate because of the same kind of Al-O sites on the mineral surfaces that form during comminution when the minerals break through their cleavage planes. Al-O sites act as active sites for collector attachment in fatty acid flotation and those active sites compete with spodumene for collector adsorption.

3.6 Mineral grades and recoveries

The target grade was reached in cleaning stages 5, 6 or 7 (CC5-CC7) depending on test conditions (Table 6). It means that with at least 12 % dilution and the current flotation procedure, the number of cleaning stages cannot be significantly reduced. The best results are in test 4 with Na₂CO₃ modifier, which reached the target grade with less cleaning stages (5th cleaning CC5) with the recovery of 85.29 %. Test 5 with twice-recycled process waters also reached the target grade in fifth cleaning, but with significantly lower recovery (81.96 %). Tests 2 and 6 reached the target grade in the sixth cleaning stage (CC6) and reference test and tests 1 and 3 in the last cleaning stage (CC7).

Table 6. Comparison of Li₂O recoveries at target grade between the tests (CC5, CC6, CC7 = cleaning stage 5, 6 or 7 respectively)

Test	Stage where target grade was reached	Li ₂ O %	Li ₂ O rec%
11	CC7	4.47	87.81

Test	Stage where target grade was reached	Li ₂ O %	Li ₂ O rec%
1	CC7	4.5	84.18
2	CC6	4.5	83.53
3	CC7	4.5	80.62
4	CC5	4.5	85.29
5	CC5	4.5	81.96
6	CC6	4.5	85.11

Mineral grade-recovery of spodumene and biotite were calculated with HSC Chemistry. The calculated modals show around 65-70 % spodumene grade in the final concentrate, while the MLA measured grade was 55 % for the reference test sample and 58 % for the test 4 sample, showing significant differences in spodumene grade. For comparison, the Li₂O recoveries at the earlier flotations were determined to be around 87-92 % depending on conditions of the test.

The trend of MgO recovery is downward with an increasing grade similar to the Li₂O trends (except for test 3). Tests 4 and 6 show the best performance at the earlier flotation's stages and tests 2, 4 and 5 in the final concentrate. Tests 4 and 6 were the best performing tests regarding Li₂O recovery and grade but tests 2 and 5 were among the worst ones so these calculated results should be taken with caution and require more comparative analysis.

Comparisons of measured Li₂O + MgO recoveries versus calculated Spd + Bt recoveries were made with each test to see if any of these results show similarities and selectivity between spodumene and biotite. Test comparisons for tests 4 and 6 are shown in Figure 8 and Figure 9. The MgO recoveries are smaller than the Li₂O. The spodumene recoveries follow the Li₂O recoveries and biotite recovery changes seem to follow spodumene trend with higher recoveries than MgO alone, which is in agreement with the variety of elements in the composition of biotite (such as Fe, Al, Si) and not only MgO.

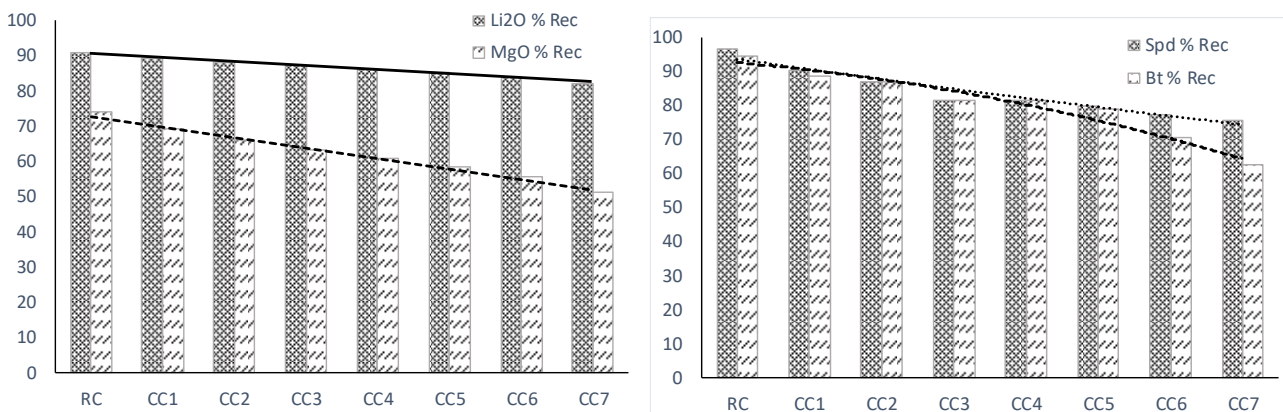


Figure 8 Test 4 recovery comparison between Li₂O + MgO vs. Spd + Bt

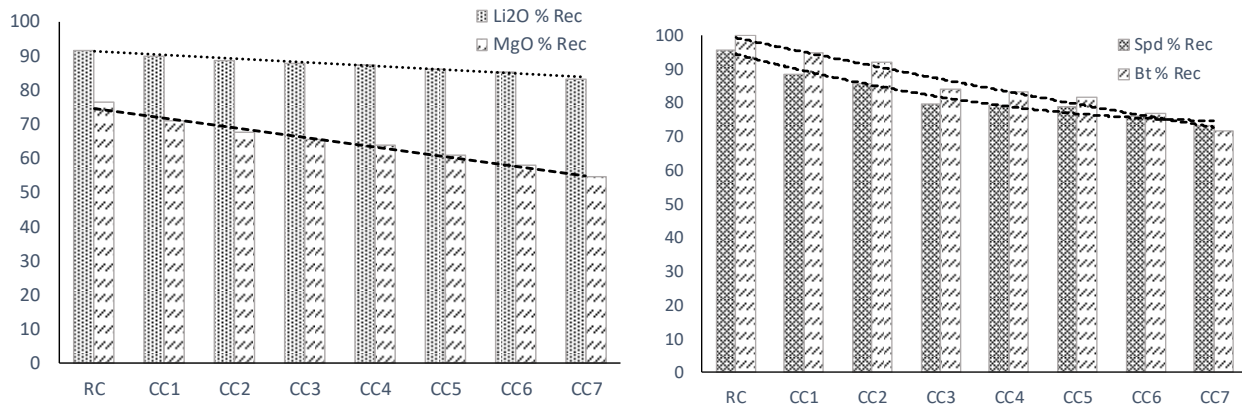


Figure 9 Test 6 recovery comparison between Li₂O + MgO vs. Spd + Bt

4. Conclusions

Magnesium-bearing minerals like biotite and amphiboles were chosen as the minerals of interest because they have proven to be the most abundant gangue mineral outside of silicate minerals that build up in the final concentrate and deteriorate the final concentrate quality. Biotite is also one of the most unwanted impurities to end up in the final concentrate regarding the metallurgical process following up the flotation enrichment since it can cause problems by promoting partial melting of the concentrate during high temperature treatment when alpha spodumene is transformed into digestible beta spodumene. Formation of the partial melt can cause agglomeration during the lithium digestion procedure, which decreases the lithium recovery and makes the process more difficult to operate. On top of Mg-bearing minerals, apatite that contains the majority of the phosphorus in the deposit is also one of the more deleterious impurities to end up in the final concentrate. Apatite is readily digestible in same conditions with beta spodumene and the main cause of P-impurities in the final lithium carbonate product.

Within this work, the test that used Na₂CO₃ as a modifier showed the most promising Li₂O grade-recovery results reaching the target grade of 4.5 % Li₂O with 85.29 % recovery already in fifth cleaning stage and ending up with final concentrate with 4.9 % grade and 82.13 % recovery. Next good results were obtained using starch as a modifier with a final concentrate of 4.73 % grade and 83.38 % recovery. However, selectivity between Mg-bearing minerals and spodumene were not attained.

Water analysis showed that increasing amounts of metal ions in the process water affect the flotation result negatively as expected. Tests done with recycled waters and the GTK pilot pond water showed the worst results regarding spodumene recovery and grade in the final concentrate. A gradual build-up of different metal ions (Ca, Na, Mg), especially in the cleaning waters show steadily decreasing flotation performance.

MLA results show that biotite contains the vast majority of the Mg between the minerals (80-90 %). Also, Mg-bearing minerals are amphiboles and chlorite. Exact amphibole minerals cannot be determined with precision, but their structure is mostly of hornblende and edenite. Biotite and amphiboles that end up in the final concentrate are mostly fully liberated, which further strengthens the theory of similar surface properties with spodumene. MgO grade-recovery curve also shows the same behavior as spodumene, but with more emphasis on slimes and preconcentrate recovery. Overall flotation results show that MgO recovery behaves the same way with Li₂O recovery in the spodumene flotation stage, which indicates that biotite and amphiboles have to some extent similar surface properties with spodumene.

For future work, tests could be performed with higher and lower reagent dosages to optimize the reagent amounts, and surface adsorption of starch should be further investigated, since in this work it seemed to produce an activating effect instead of depressing effect, which was the opposite of the initial assumption with spodumene according to the literature.

Since the main difference between the spodumene and biotite recoveries is the greater recovery of biotite in slimes and preconcentrate, both still mostly build up in the final concentrate, some emphasis could be done in developing desliming and preflotation stage to possibly increase biotite recovery. In addition, surface studies on samples from recycled process water tests are suggested to determine what chemical species and mechanisms are causing the decreased recoveries and furthermore try to remove them efficiently since process water recycling will be almost mandatory in the future.

5. Acknowledgements

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