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Tiago da Cruz Pinto

**OPTIMIZATION OF SPODUMENE ORE BLEND FLOTATION: (RE)USE OF
TAILINGS DAM**

**OTIMIZAÇÃO DA FLOTAÇÃO DE MINÉRIO BLENDADO DE ESPODUMÊNIO:
(RE)APROVEITAMENTO DE BARRAGEM DE REJEITOS**

Belo Horizonte
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(re)aproveitamento de barragem de rejeitos**

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EPIGRAPH

“Those worlds in space are as countless as all the grains of sand on all the beaches of the earth. Each of those worlds is as real as ours and every one of them is a succession of incidents, events, occurrences which influence its future. Countless worlds, numberless moments, an immensity of space and time. “

*- Carl Sagan
Cosmos: A Personal Voyage (1990).*

RESUMO

O minério de lítio tem tido uma valorização exponencial nos últimos anos devido as suas aplicações na indústria automotiva em produção de baterias, especificamente, baterias de íon-lítio (*LIBs*). O lítio pertence a um grupo seletivo de minerais, como o cobalto, cobre, grafite, nióbio, níquel, entre outros, considerados minerais estratégicos devido as suas diversas aplicações como na produção de diversos tipos de baterias com cátodos do tipo $\text{LiNi}_x\text{Co}_y\text{Al}_z\text{O}_2$, $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$, LiMn_2O_4 , entre outros. As *LIBs* são usadas para alimentar a indústria emergente de veículos elétricos (EV) e híbridos (HEV) que tendem a observar um crescimento significativo, principalmente no Brasil, onde é esperado que ao longo dos próximos 10 anos poderá superar 1,8 milhões de unidades, o que implica uma maior demanda por matérias-primas. Assim sendo, a crescente demanda recuperação de minérios cada vez mais pobres e/ou oriundos de barragens de rejeitos e de forma mais sustentável tem sido motivo para estudos de otimização de processos a partir de estudos de redução de coletores e maximização das recuperações mássicas e metalúrgicas de minérios blindados com 50/50% de rejeitos de uma planta de tântalo e de barragem de rejeitos. O modelamento matemático da flotabilidade em função da faixa granulométrica e mineralogia permitirá entender melhor os fenômenos de flotação e arraste mecânico empregados na flotação de minérios finos de lítio e minerais de ganga. O presente trabalho tem como objetivo propor um estudo de otimização da flotação do minério de lítio para atingir um produto comercializável ($>5,5\%$ Li_2O) visando a simulação do processo de flotação em escala de bancada. A liberação do espodumênio é dada em fração em torno de $250\text{ }\mu\text{m}$, sendo que as frações finas ($-150+38\mu\text{m}$) empregam minerais mais liberados e com elevada área superficial específica. O minério blendado é composto por majoritariamente albita (41.8%), quartzo (37.2%), espodumênio (11.4%) e traços de microclina (0.1%) e muscovita ($<0.1\%$). O resultado ótimo para um único estágio de flotação rougher foi alcançado com 5,34% e 58,60% de teor e recuperação de Li_2O e 1,92% e 25,58% de teor e recuperação de Fe_2O_3 . E para uma segunda fase, a flotação mais limpa, o grau e a recuperação de 5,90% e 60,32% de Li_2O , seguidos por 1,12% e 34,54% de grau e recuperação de Fe_2O_3 . A recuperação global foi de 78,71% de Li_2O e 17,31% de Fe_2O_3 .

Palavras-chave: minério de lítio; baterias de íon-lítio; flotação; modelamento; otimização; planejamento fatorial.

ABSTRACT

Lithium ore has experienced an exponential valuation in recent years due to its applications in the automotive industry in the production of batteries, specifically, lithium-ion batteries (LIBs). Lithium belongs to a selective group of minerals, such as cobalt, copper, graphite, niobium, nickel, among others, considered strategic minerals due to their various applications as in the production of various types of batteries with cathodes such as $\text{LiNi}_x\text{Co}_y\text{Al}_z\text{O}_2$, $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$, and LiMn_2O_4 , among others. The LIBs are used to feed the emerging industries of electric (EV) and hybrid vehicles (HEV) that tend to observe a significant growth, especially in Brazil, where it is expected that over the next 10 years may exceed 1.8 million units, which implies a greater demand for raw materials. With this note, the increasing demand for more efficient recovery of poorer ores and/or from tailings dams and with a more sustainable way as motivated studies for process optimization through collector reduction and, mass and metallurgical recovery maximization of blended ores with 50/50% composition from tantalum tailing plant and tailings dam. The mathematical modelling of floatability, metallurgical recovery, and grade with the use of factorial design will allow a better understanding of the phenomena of flotation of blend spodumene ore. The present work intends to propose a study of lithium ore flotation optimization to reach a marketable product ($>5.5\%$ Li_2O) aiming the simulation of flotation process in bench scale. The spodumene liberation is foreseen around $250\mu\text{m}$ fraction, where the finer fraction ($-150+38\mu\text{m}$) group more liberated minerals and with higher specific surface area. The blended ore is composed of majority albite (41.8%), quartz (37.2%), spodumene (11.4%) and traces de microcline (0.1%) e muscovite ($<0.1\%$). The optimal result for a single stage rougher flotation was achieved 5.34% and 58.60% Li_2O grade and recovery and 1.92% and 25.58% Fe_2O_3 grade and recovery. And for a second stage, cleaner flotation the 5.90% and 60.32% Li_2O grade and recovery, followed by 1.12% and 34.54% Fe_2O_3 grade and recovery. The global recovery was of 78.71% of Li_2O and 17.31% of Fe_2O_3 .

Keywords: lithium ore; lithium-ion batteries; flotation; modelling; optimization; design of experiments.

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1. INTRODUCTION

In midyear 2021, the Brazilian government on the 2nd Resolution (BRASIL, 2021) classified cobalt, copper, graphite, niobium, nickel, and lithium ores as highly important mining products due to their high technology and diverse applications. Such as, production of glass, ceramics, lubricant, grease manufacturing, pharmaceutical and rubber industries, to air conditioning and dehumidification systems, and usage in lithium ion battery, where the latter has shown a trend due to the booming of the electric automobiles industry, increasing by 13% over years 2005 to 2017 (TADESSE et al., 2019; YELATONTSEV; MUKHACHEV, 2021), where Chile and Argentina are the major reserves and producers from brines and hard rock, respectively, followed by minor producers such as Canada, Zimbabwe, Portugal and Brazil. Summarizing, a total production, and reserves of over 100,000 million tonnes of lithium concentrate and 22,000,000 million tonnes, respectively, from whom Brazil contributes with about 1,500 and 95,000 million tonnes, respectively (USGS, 2022). With a price of battery-grade lithium carbonate over 13,900 USD/t in 2017 (TADESSE et al., 2019) to about 77,000 USD/t in May 2022 (CANARY MEDIA, 2022), depicting a boost of more than 550% in just 5 years, however from 2022 prices decreased.

According to DUARTE CASTRO; CUTAIA; VACCARI (2021), it's expected by 2030 that the Brazilian market will surpass 1.8 million units of electric cars resulting in the increasing demand for crucial raw materials like lithium, cobalt, nickel, manganese, and graphite by 8,700, 15,000, 46,000, 15,000 and 92,000 tonnes, respectively. After promulgation of the Law that would see tax exemptions over industrialized products of foreign origin and financial transactions tax (IOF), in 2019, there was a high demand for electric and hybrid vehicles in the country with a development reaching 198% compared to the previous year.

Lithium is used as an anode in lithium-ion batteries (LIBs) industry powering new sustainable electric vehicles (EV) and hybrid vehicles (HEV) in with several cathode types, for example $\text{LiNi}_x\text{Co}_y\text{Al}_z\text{O}_2$ (NCA), $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ (NCM or NMC), LiMn_2O_4 (LMO) and LiFePO_4 (LFP) (DUARTE CASTRO; CUTAIA; VACCARI, 2021). CASTELVECCHI (2021) estimates that a single EV with an NMC battery pack contains just over 8 kg of lithium, 35 kg of nickel, 20 kg of manganese and 14 kg of cobalt, about 77 kg of raw elements.

The global production of lithium ore occurs in only two economic sources, over 60% are from brines and approximately 40% from hard rock, specifically from lithiferous pegmatite deposits in the form of spodumene, petalite, lepidolite, amblygonite, zinnwaldite, eucryptite and triphylite with 4.5-8.0 %, 3.0-4.7 %, 1.2-5.9 %, 7.4-9.2 %, 3.3-7.7 %, 4.5-6.5 % and 4.4-9.7 % Li_2O content, respectively (RAJU, 2022). The lithium carrier pegmatites are accompanied by sub products like columbite-tantalite, beryllium, tourmalines, and gangue minerals such as albite, microcline, plagioclase and other aluminosilicates micas and minerals (ASSUMPÇÃO, 2015).

Over the life span of the mine there is an increase in the production rate but a decrease of ore grade. Usually, the enriched ore tends to decrease as the depth increases from which conventional concentration processes become inefficient, making miners seek for alternative concentration methods for fine and ultrafine particles. Flotation is a method that allows for concentration of fine particles (< 1 mm) that would be discarded as tailings in tailings dams (VIANA,

2006) or dry stacked (TESSAROTTO, 2015), however, as explained by FARROKHPAY, FILIPPOV and FORNASIERO (2021) in recent year low-grade deposits have gain economical value making fine particle flotation highly important, however, it is also a crucial due to environmental issue such as acid mine drainage. Furthermore, the best-known conditions for particle flotation are mainly in the range between 15 and 150 μm , above it too coarse to be carried by the air bubbles and below it it's too thin and with high electronegative (surface) energy to be adsorbed by the air bubble and elevated specific surface (area) to be consumption of reagents, respectively, as a result there is a low recovery rate (SOMASUNDARAN, 1980).

All things considered, this work aims to achieve a more efficient metal recovery with low consumption of chemical reagents, by spodumene optimizing of blended ores from tantalum tailings from processing plant and from a tailings dam.

2. INTRODUÇÃO

Em meados de 2021, o governo brasileiro na sua 2ª Resolução classificou os minérios de cobalto, cobre, grafite, nióbio, níquel e de lítio como produtos de mineração de grande importância devido às suas altas tecnologias e aplicações diversificadas. Tais como fabricação vidro, cerâmica, lubrificantes, fabrico de graxas, indústria farmacêutica e de borracha, para sistemas de ar condicionado e desumidificação, e utilização em baterias de íons de lítio, onde este último, observou um aumento de 13% em relação aos anos de 2005 a 2017 (TADESSE *et al.*, 2019; YELATONTSEV; MUKHACHEV, 2021), onde o Chile e a Argentina detêm as maiores reservas e produções de salmoura e rocha dura, respectivamente, seguidos por produtores menores como Canadá, Zimbábue, Portugal e Brasil. Resumindo, uma produção total e reservas de mais de 100.000 milhões de toneladas de concentrado de lítio e 22.000.000 milhões de toneladas, respectivamente, dos quais o Brasil contribui com cerca de 1.500 e 95.000 milhões de toneladas, respectivamente (USGS, 2022). Com o preço de carbonato de lítio, com especificação para uso em baterias, superior a 13.900 USD/t em 2017 (TADESSE *et al.*, 2019) para cerca de 77.000 USD/t em maio de 2022 (CANARY MEDIA, 2022), representando uma valorização de mais de 550% em apenas 5 anos.

De acordo com DUARTE CASTRO; CUTAIA; VACCARI (2021), espera-se que até 2030 o mercado brasileiro ultrapasse 1,8 milhões unidades de carros elétricos, resultando na crescente demanda por matérias primas cruciais como lítio, cobalto, níquel, manganês e grafite em 8.700, 15.000, 46.000, 15.000 e 92.000 toneladas, respectivamente. Após a promulgação da Lei que preveem isenções fiscais sobre produtos industrializados de origem estrangeira e imposto sobre transações financeiras (IOF), em 2019, houve uma alta demanda por veículos elétricos e híbridos no país, que atingiu 198% de aumento quando comparado com o ano anterior.

O lítio é usado como anodo na indústria de baterias de íon-lítio (LIB's), alimentando novos veículos elétricos (EV) e veículos híbridos (HEV) sustentáveis com vários tipos de cátodos, por exemplo, $\text{LiNi}_x\text{Co}_y\text{Al}_z\text{O}_2$ (NCA), $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ (NCM ou NMC), LiMn_2O_4 (LMO) e LiFePO_4 (LFP) (DUARTE CASTRO; CUTAIA; VACCARI, 2021). CASTELVECCHI (2021) estima que um único EV com uma bateria NMC contém pouco mais de 8 kg de lítio, 35 kg de níquel, 20 kg de manganês e 14 kg de cobalto, cerca de 77 kg de elementos brutos.

A produção global de minério de lítio ocorre em apenas duas fontes econômicas, mais de 60% são de salmoura e aproximadamente 40% de rocha dura, especificamente de depósitos de lítio pegmatítico na forma de espodumênio, petalita, lepidolita, ambligonita, zinnwaldita, eucryptita e trifilita com 4,5 – 8,0 %, 3,0 – 4,7 %, 1,2 – 5,9 %, 7,4 – 9,2 %, 3,3 – 7,7 %, 4,5 – 6,5 % e 4,4 – 9,7 % de Li_2O , respectivamente (RAJU, 2022). Os pegmatitos portadores de lítio são acompanhados de subprodutos como columbita-tantalita, berílio, turmalinas e minerais de ganga como albita, microclina, plagioclásio e outras micas e minerais de aluminossilicatos (ASSUMPÇÃO, 2015).

Durante a vida útil da mina há um aumento na taxa de produção, mas uma diminuição do teor de minério. Normalmente, há tendências de que minério enriquecido diminuem à medida que aumenta a profundidade a partir da qual os processos convencionais de concentração se tornam ineficientes, fazendo com que as mineradoras busquem métodos alternativos de concentração

para partículas finas e ultrafinas. A flotação é um método que permite a concentração de partículas finas ($< 1\text{mm}$) que seriam descartadas como rejeitos em barragens de rejeitos (VIANA, 2006) ou empilhadas à seco (TESSAROTTO, 2015), entretanto, como explicado por FARROKHPAY, FILIPPOV e FORNASIERO (2021) nos últimos anos depósitos de baixo teor ganharam valor econômico tornando a flotação de partículas finas altamente importante, entretanto, ela também é fator crucial devido a questões ambientais tais como drenagem ácida de minas. Além disso, as melhores condições para flotação de partículas são principalmente na faixa entre 15 e 150 μm , acima são muito grossas para serem levada pelas bolhas de ar e abaixo são muito fina e com alta energia eletrônica (de superfície), para ser adsorvida pela bolha de ar, e elevada (área) superfície específica no consumo de reagentes. E como resultado, há uma baixa taxa de recuperação (SOMASUNDARAN, 1980).

Levando tudo em consideração, este trabalho visa uma recuperação mais eficiente e de baixo consumo de reagentes químicos, pela qual, há uma necessidade de otimização da flotabilidade de espodumênio em minérios blindados dos rejeitos da usina de processamento tântalo e das barragens de rejeitos.

3. GENERAL OBJECTIVE

This study aims on the optimization of a blended spodumene ore recovery by variation of process conditions from a bench scale flotation.

1.1 SPECIFIC OBJECTIVES

The specific objectives of this master's thesis consisted of:

- Chemical, mineralogical and granulometric characterization of lithium blend.
- Assessment of granulometric and mineralogic floatability of spodumene and gangue particles.
- Development and optimization of flotation model.

4. LITERATURE REVIEW

1.2 LITHIUM ORE

1.2.1 Geological and Mineralogical Review

According to YOUNG (2019), in 1817 while try to identify the chemical composition of petalite mineral components, Johan August Arfwedson identified and named *lithion* after *lithos*, the Greek word for stone, that showed to presented similar properties to sodium and potassium. Lithium a chemical element, shown in Figure 4-1, the 3rd atomic number with two natural occurring isotopes with atomic masses of 6 and the most abundant (92.5%) isotope with 7 and atomic weight of 6.94 amu or g.mol⁻¹.

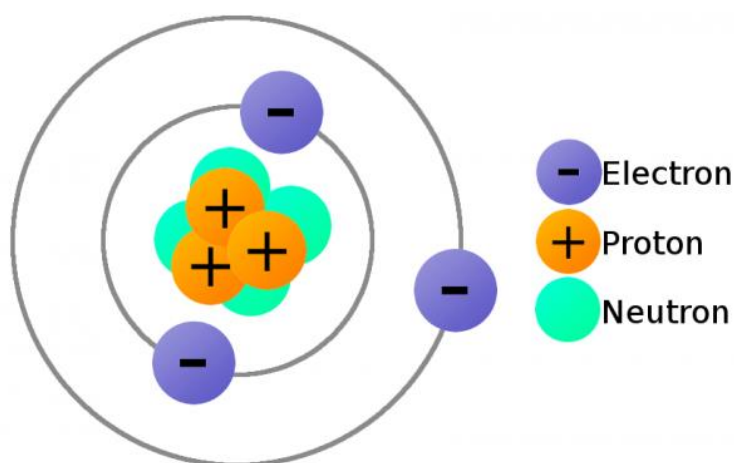


Figure 4-1: Lithium atomic structure.

Furthermore, lithium is naturally occurrent as a monovalent cation associated with sodium, potassium, rubidium, and caesium as part of the alkali metal group, with high grade of purity it's a soft and silvery metal bright, with relative low density (0.534 g/cm³).

After its discovery it was found that lithium was also present in other minerals such as spodumene and zinnwaldite. And in 1821 was isolated as pure element and electrolyzed as lithium oxide, afterwards electrolyzed in the form of lithium chloride in 1855 which led to the industrial-scale production of lithium in 1923.

Around 150 minerals have been identified to contain lithium on crystallographic structure, but the majority are classified as lower-grade Li-bearing minerals. As formerly cited, lithium is found in a vast number of minerals however only limited group of aluminosilicate minerals as spodumene, lepidolite, amblygonite, zinnwaldite and petalite, and in brines have the economic value to be characterized as mineral-ore (BRAGA; SAMPAIO, 2008; FILIPPOV *et al.*, 2019).

Table 4-1: Main economic lithium bearing minerals, structure, hardness and %Li₂O content.

Minerals	Formula	Density	Hardness	% Li ₂ O content	Group
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		(g/cm ³)		Theoretical	Typical	
Amblygonite	$\text{LiAl}(\text{PO}_4)(\text{F},\text{OH})$	3	5.5 – 6	11.9	5.0	Amblygonite
Eucryptite	$\text{LiAl}(\text{SiO}_4)$	2.6	6.5	11.9	5.0	Phenakite
Lepidolite	$\text{K}(\text{Li},\text{Al})_3(\text{Si},\text{Al})_4\text{O}_{10}(\text{F},\text{OH})_2$	2.8 – 3.3	2.5 – 3	3.3 – 7.8	3.0 – 4.0	Mica
Montebrasite	LiAlPO_4F	3.0	5.2 – 6.0	7.0	–	Amblygonite
Petalite	$\text{LiAl}(\text{Si}_4\text{O}_{10})$	2.3 – 3.2	6 – 6.5	4.9	3.0 – 4.7	Phyllosilicate
Spodumene	$\text{LiAl}(\text{Si}_2\text{O}_6)$	3.0 – 3.2	6.5 – 7.5	8.0	1.0 – 7.7	Pyroxene
Hectorite	$\text{Na}_{0.3}(\text{Mg},\text{Li})_3\text{Si}_4\text{O}_{10}(\text{OH})_2$	2.3	1.0 – 2.0	4.3 – 10.7	0.4 – 0.7	Clay
Zinnwaldite	$\text{K}(\text{Li},\text{Al},\text{Fe})_3(\text{Al},\text{Si})_4\text{O}_{10}(\text{F},\text{OH})_2$	2.9 – 3.3	2.5 – 4.0	5.6	2.0 – 5.0	Mica

Source: Adapted from BRAGA; SAMPAIO, (2008); YOUNG, (2019).



Figure 4-2: Crystallized minerals of (A) Spodumene, (B) Amblygonite, (C) Eucryptite, (D) Petalite, (E) Montebrasite and (F) Zinnwaldite.

Source: mindat.org

According to YOUNG (2019), most of the mineral shown in Table 4-1 represent the major economic deposits for hard rock pegmatites, however, hard rock are a minority lithium deposit sources while the majority of deposits are found in brines from evaporites (see chapter 1.2.2 Global Market Present & Future). The ore processing of brines and lithiferous pegmatites will be presented in chapters 1.2.4.1 and 1.2.4.2, respectively.

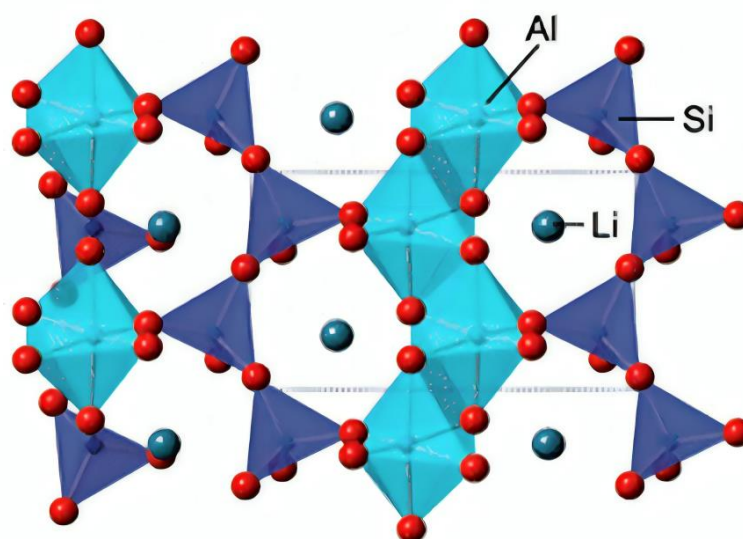


Figure 4-3: Crystallographic structure of spodumene (red ball – oxygen, green ball – lithium).

Sources: FILIPPOV *et al.*, (2019).

Spodumene (Figure 4-2 Figure 4-2: Crystallized minerals of (A) Spodumene, (B) Amblygonite, (C) Eucryptite, (D) Petalite, (E) Montebrazite and (F) Zinnwaldite.& Figure 4-3) is the main lithium ore mineral for extraction from hard rock ore bodies such as granitic pegmatites (VIANA, 2006) with just over 8.03% Li_2O 64.58% SiO_2 and 27.40% Al_2O_3 , content and is usually associated to gangue minerals such as quartz, feldspar, micas, etc. Spodumene presents inosilicate structure with a monoclinic crystal system with a series of single-chain silica tetrahedrons and that are bonded together by sharing some oxygen between two other tetrahedrons generally Si^{4+} or Al^{3+} (VIANA, 2006).

New surfaces are generated from grinding consist of breaking of Si-O and Al-O bonds, with the latter having a longer bond when compared to the former, however there isn't enough strength to formation bonds of lithium and oxygen (FILIPPOV *et al.*, 2019; XIE *et al.*, 2021). VIANA (2006) elucidates that Li^+ and Al^{3+} ions can occupy sites alongside octahedral coordination. While XU *et al.*, (2016) was evaluating the adsorption of sodium oleate (NaOL) on different particle size spodumene fractions they found that there is a difference in bond breakage depending on the surface plane, generating different density of broken surface bonds for Al-O, Si-O and Li-O (Figure 4-4).

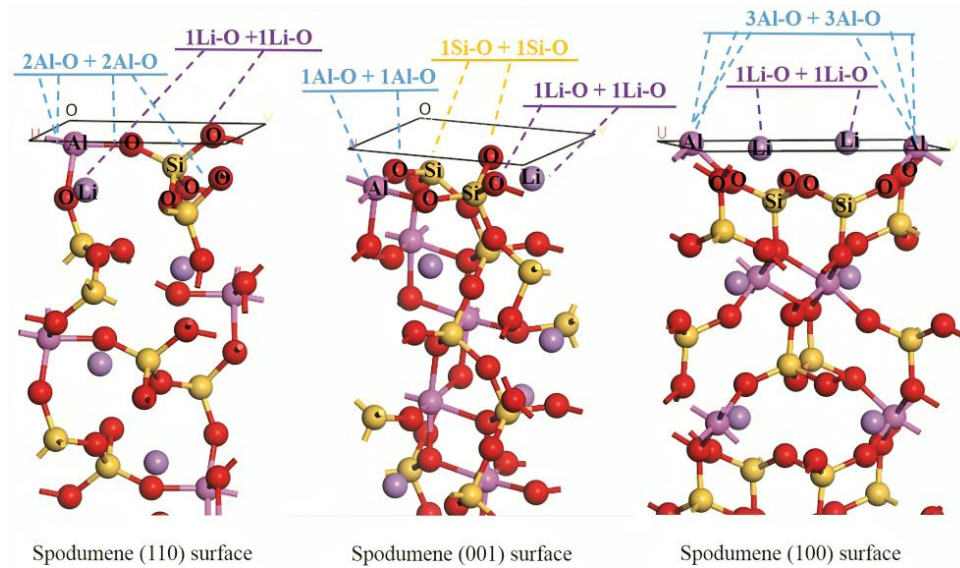


Figure 4-4: Spodumene surface broken bonds schematic.

Source: XIE et al., (2021) apud XU, (2016).

The difference on type of bond broken density will have severe impact in the adsorption of different collectors, aggregation, and flotation of spodumene which will be explained with more details on chapter 1.3.3. Spodumene can vary with temperature and pressure gradient, as depicted in Figure 4-5. From 200° to 750° C occurs crystallization of spodumene, being from 300 – 500 MPa and between 500° to 650° C the is the formation of primary α -spodumene crystals (ASSUMPÇÃO, 2015), whereas at low pressure there is the crystallization of petalite which more liquidus phase and contains about 2.0 wt.% of Li_2O (SIMMONS, 2007) and a rare phase such as β -spodumene if not formed naturally and γ -spodumene or virgilite is a very rare phase (DESSEMOND et al., 2019).

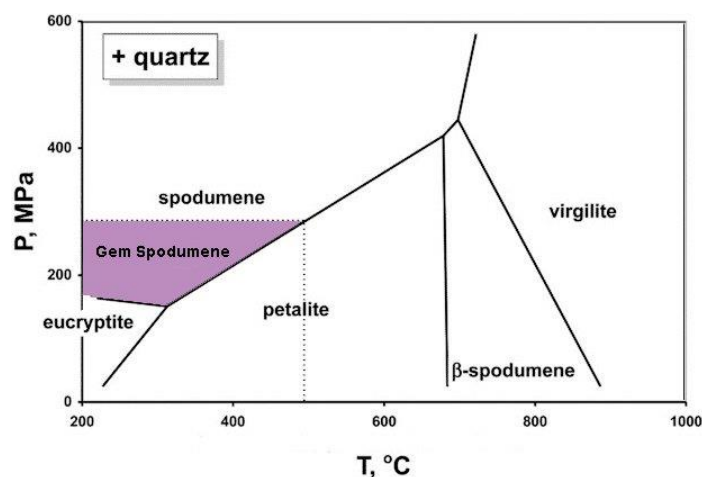


Figure 4-5: Li-bearing minerals formation by varying pressure and temperature gradient.

Source: SIMMONS, (2007).

The main granitic pegmatite formation found in Brazil occurs in the Oriental Pegmatitic Province with 150,000 km² situated between four states, namely, Minas Gerais, Bahia, Espírito

Santo, and Rio de Janeiro within the São Francisco Craton. With a predominance of volcano-sedimentary rock formation in coherence with greenstone belt¹ structure (CHAVES, DIAS, CARDOSO, 2018; ASSUMPÇÃO, 2015).



Figure 4-6: South America geological makeup.
Source: Del, (2018).

There are four (4) known lithium deposits or occurrences of lithium in the state of Minas Gerais, in the counties of Araçuaí-Itinga, Conselheiro Pena-Divino das Laranjas, Santa Maria do Suaçuí and São João del Rei, bearing over 56 mines and artisanal mining in diverse status such as active, inactive, intermittent, paralysed, and exhausted. There are at least 3 major mining companies operating, as noted Brazilian Lithium Company (CBL) and Sigma Lithium Mining in Araçuaí/Itinga region and AMG Brazil in São João Del Rei Pegmatite District (area of 1,400 km²) (CHAVES; DIAS; CARDOSO; 2018) dating over 2,267 to 2,223 million years (Ma) and 1.531 to 1.54 billion years (Ga) (ASSUMPÇÃO, 2018).

¹ **Greenstone belt** – are metamorphosed volcanic and sedimentary rocks with large scale structures, usually elongated, formed in the Archean and Proterozoic cratons constituted from granitoids and gneiss formations (ARNDT, 2011).



Figure 4-7: Known lithium-bearing deposits or occurrences in the state of Minas Gerais: (1) Araçuaí-Itinga; (2) Conselheiro Pena-Divino das Laranjas; (3) Santa Maria do Suaçuí and (4) São João Del Rei.
Sources: CHAVES, DIAS, CARDOSO, (2018).

The spodumene mine, situated in the São João Del Rei Pegmatite Province, is characterized with large pegmatite bodies enriched spodumene (10 – 15%) of the overall body. Granitic pegmatites in the mine region have been found to contain minerals such as beryl, amblygonite, spodumene, columbite-tantalite, apatite, and monazite, but the plant feed can vary with other minerals as albite, microcline, muscovite and holmquistite (SOARES, 2021). The main ore of the mine is set at the Body A (Corpo A), in Figure 4-8, with tabular sub-horizontal elongation in the EW direction, medium dip of 27°, thickness between 18 and 25 meters and about 1,000 meters of extension (ASSUMPÇÃO, 2018).

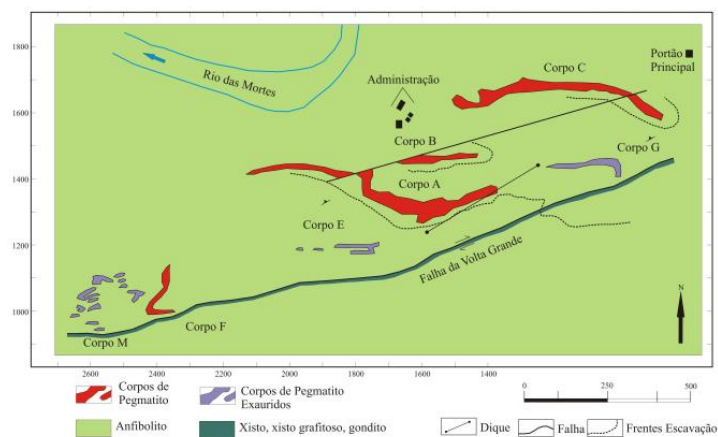


Figure 4-8: Lithostructural map of the mine area with description of the diverse pegmatite bodies.
Source: ASSUMPÇÃO, (2018).

1.2.2 Global Market Present & Future

According to the USGS Report (2022), lithium bearing minerals can be extracted from three know sources, namely, brines-based, mineral-based, and clay-based, whereas most lithium if

produced from brines from the South Americas such essentially from Argentina and Chile, followed by Australia and China. Other sources can be found in Li-bearing-pegmatites with minor production from Brazil, Portugal, China, Zimbabwe and from sedimentary clay under development in Mexico and United States. DESSEMOND *et al.*, (2019) estimates that there is over 62 Mt of lithium resources over the globe from brines and ore mineral from which 14 Mt (22.6%) derived from the letter.

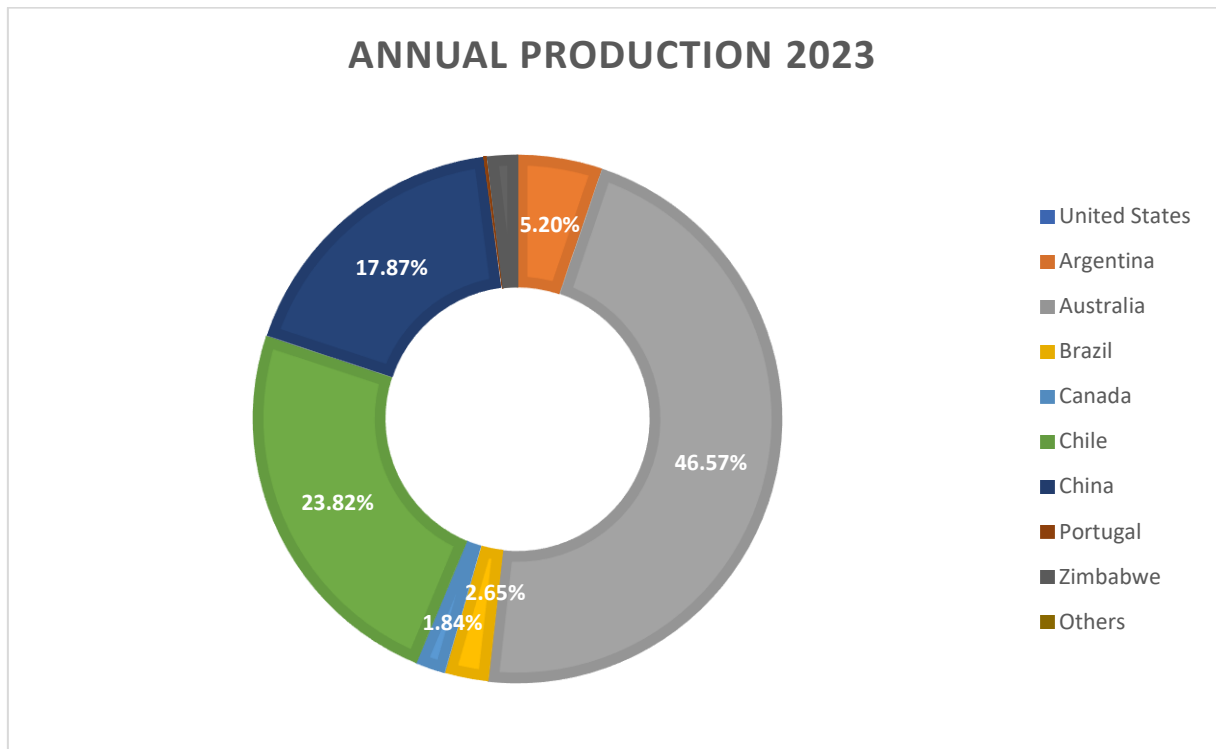


Figure 4-9: Global lithium production in 2023.
Source: Adapted from USGS Report, (2024).

Australia (46.6%), Chile (23.8%) and China (17.9%) account for more about 90% of the global production of a total of 180,000 million tons (163,293.00 million metric tons), 27% increase when compared to the 2022 production. Brazilian contribution to the global production in 2023 was just slightly above 2.7%, however it also observed an increase of 86.3% between 2022 and 2023, from 2,630 to 4,900 million tons, respectively. It's important to note that other producers like the United States and Congo did not share their annular production so it was not counted in the Annual Production 2024 (Figure 4-10).

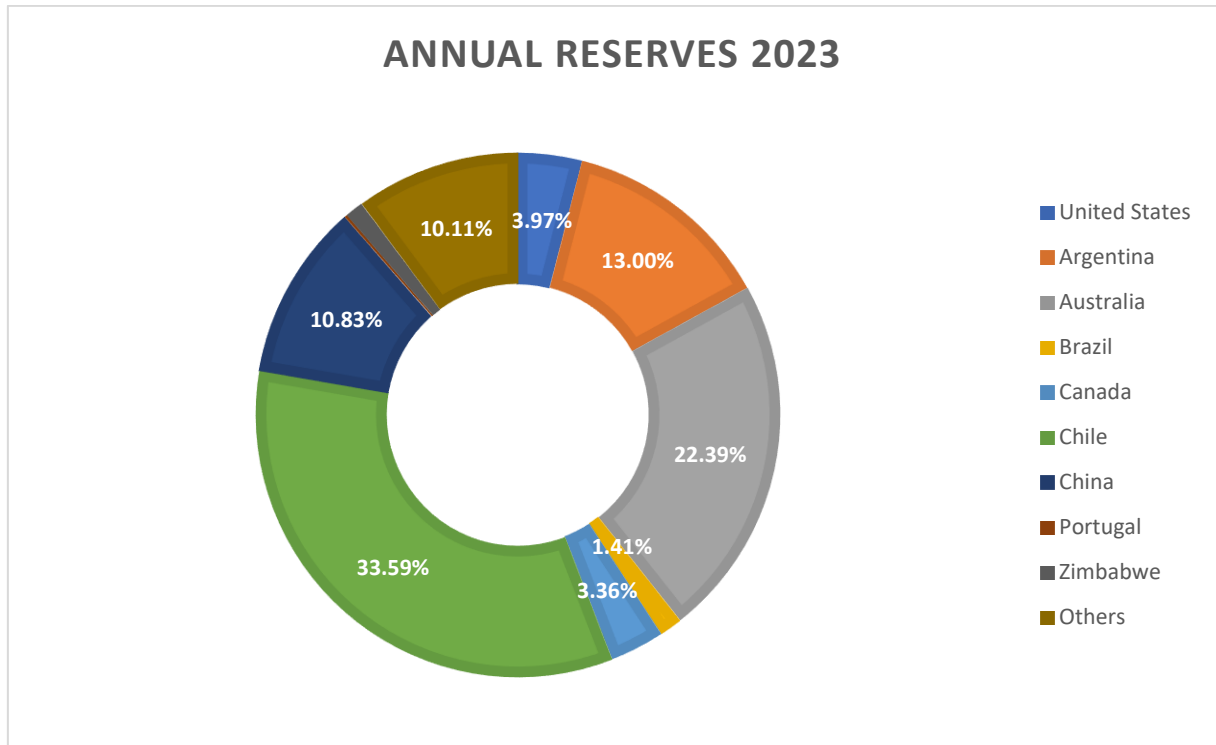


Figure 4-10: Global lithium reserves in 2023.
Sources: Adapted from USGS Report, (2024).

On the other hand, Chile (33.6%) and Australia (22.4%) account for more than half (56.0%) of the total global reserves (28,000,000 tons or 24,493,987.98 metric tons). Brazil contributes with 1.41%, however countries like Argentina have a more impactable reserve (13.0%).

Lithium and lithium by-products have a diverse usage range, from ceramics and glass production (4%), air treatment (1%) and lubrication of greases (2%) more than 80% of all lithium production is used in the production of lithium-ion batteries (LIBs) as shown in Figure 4-11.

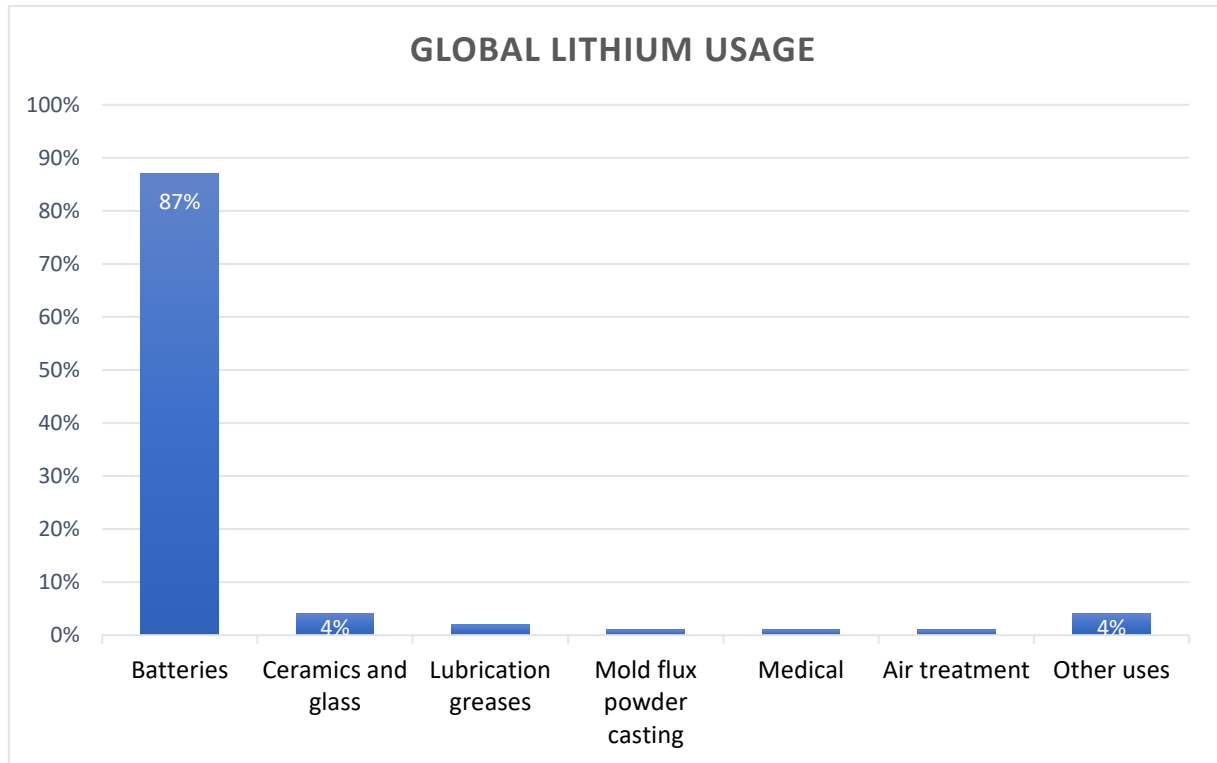


Figure 4-11: Global usage of lithium distribution by industry.

Source: USGS Report, (2024).

However, the usage varies from the primary source. As DESSEMOND *et al.*, (2019) demonstrates in Figure 4-12, some applications such as inorganic compounds can only be produced from lithium hydroxide, just as, rubber from butyllithium or Al-Li alloys from metallic lithium. In contrast, almost all intermediate compounds can be used in the production of LIBs and is in coherence with the global usage Figure 4-11.

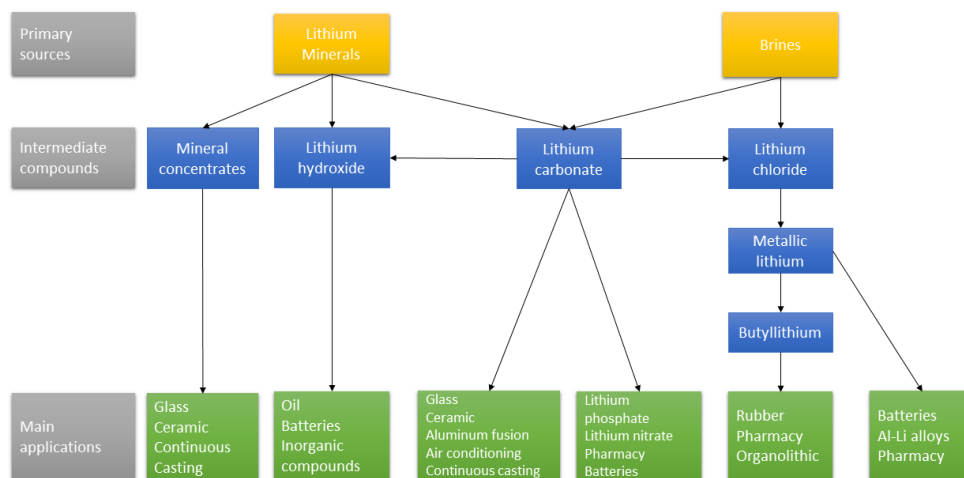


Figure 4-12: Diagram of lithium usages by various sources.

Source: Adapted from DESSEMOND *et al.*, (2019).

The price of lithium intermediate compounds varies by type and final product. The price of lithium carbonate in U.S. dollars per metric ton (\$/t) of battery-grade lithium has grown exponentially over the past two (2) years, booming from 8,000 to 75,000 \$/t, from 2020 to 2022, respectively, this presents a growth of 937.5%.

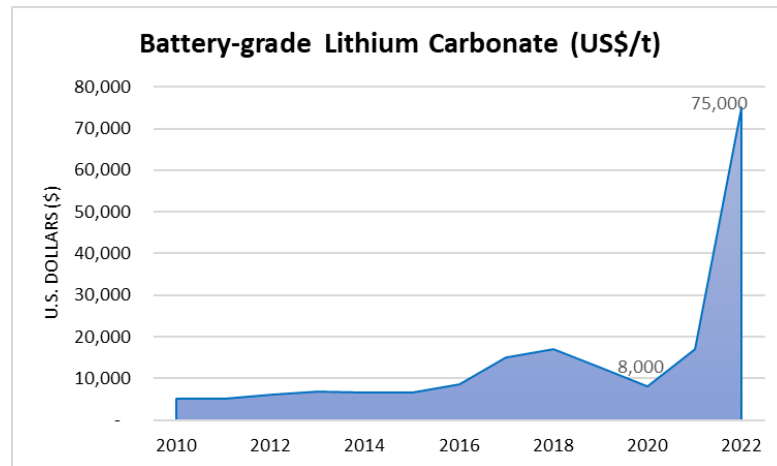


Figure 4-13: Lithium carbonate market price in American dollar per metric ton (US\$/t) over the years.
Source: Adapted from CANARY MEDIA, (2022).

These trends can also be seen in the Chinese market as shown in Figure 4-14 where lithium carbonate had a significant growth of 644,8% from 2020 to 2022, increase from 91,885.4 to 592,500 (in 16/11/2022) Chinese Yuan per metric ton (CNY/t), respectively, equivalent to 12,841.23 to 82,803.43 US\$/t (with exchange rate of 1 CNY = 0.14 US\$). In 2024 the lithium prices went down significantly 79,500 CNY/t, equivalent to 11,164.48 US\$/t.

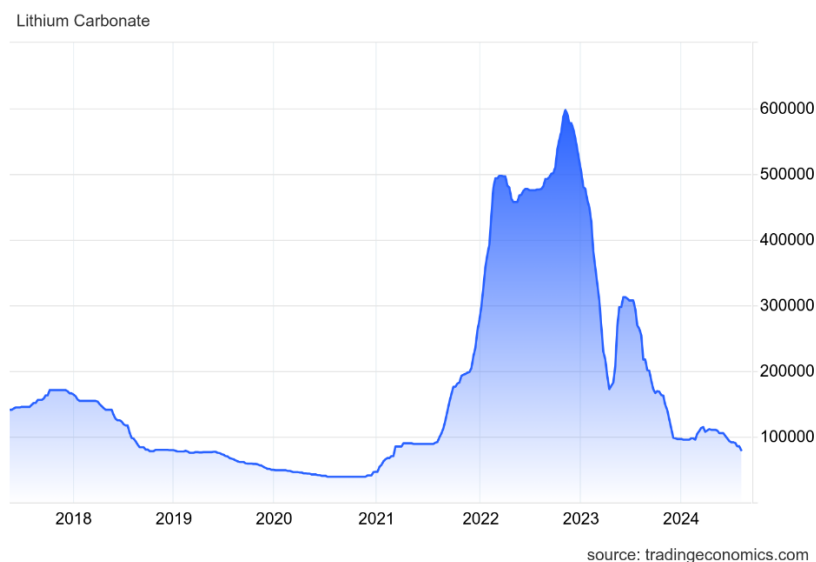


Figure 4-14: Market price for lithium carbonate in (CNY/T).

Publish at: 05/08/2024.

Source: TRADING ECONOMICS, (2024).

Figure 4-15 show the major spikes in lithium intermediate compounds prices over the past few years where can be noticed that has been a significant increase in prices of spodumene

concentrate 6% Li_2O (532%), lithium carbonate (431%) and lithium hydroxide (340%) in an extent of a year (NEWSFILE, 2022).

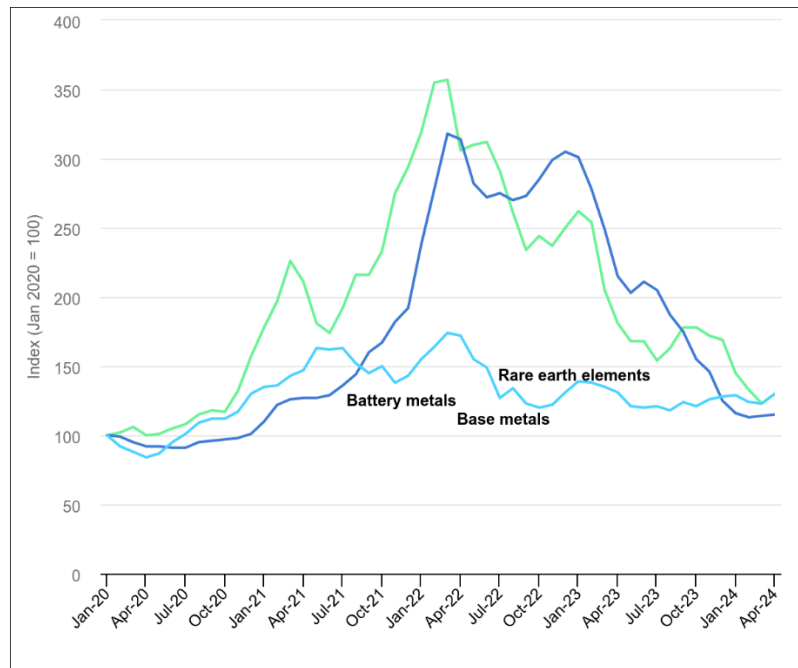


Figure 4-15: Mineral prices developments of base metals, rare earth elements and battery materials.

Publish at: 17/04/2024.

Source: IEA, 2024.

On the other hand, over the past half year other battery mineral such as nickel and cobalt have seen a decrease in market prices compared to lithium that from the end of 2021 to mid-year 2022 have raised to 70%. Nickel prices have seen fluctuation over this first semester and have risen to 53% and afterwards down to 8% with market value of 22,499 US\$/t. The same can be seen for cobalt that on May trends until June and went down to over 32US\$ per pound (US\$/£) (Batteries News, 2022).

Lithium prices refuse to come down

Dec. 31, 2021 = 100

■ Nickel ■ Lithium ■ Cobalt

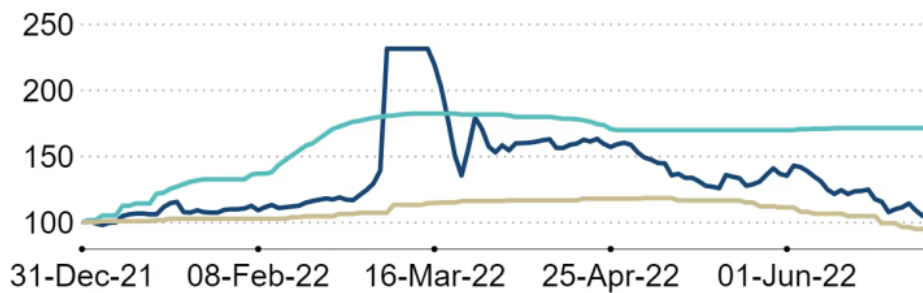


Figure 4-16: Lithium, nickel and cobalt prices over the first semester of 2022.

Source: REDACTORAMEXICO, (2022).

1.2.3 Lithium-ion Batteries (LIBs)

As the world progresses to the use of new renewable energies the need of more efficient storage units follows along. For a long time, sealed lead-acid (SLA) batteries dominated the global battery market and still does (U.S. DEPARTMENT OF ENERGY, 2020).

BUCHMANN (2018), explains that the invention of the first commercial usage rechargeable lead-acid battery was the work of *Gaston Planté*, in 1859, and had gain popularity due to is cheap, dependable, and low-cost-per-watt prices and budget efficiency for automobiles, cars, uninterruptible power supplies and other usages. However, lead-acid batteries have a low life cycles assessment (LCA) over 200 to 300 for deep-cycles (for discharging and recharging) and with every new recharging is has a loss of capacity due to sulphation that adds carbon on the negative electrodes and a full recharged battery can take up to 16 hours. Up to a point these were the most efficient batteries, now new more efficient batteries have emerged that have instigated a new battery dominance race.

The functionality of a battery (seen in Figure 4-17) consists of two electrodes, one with a negative charge (anode) and another with positive charge (cathode) on opposite ends, separated by a semipermeable layer of electrolyte that prevents electrons from passing from positive-to-negative in the short-circuit but accepting passage of cations from the positive-to-negative and vice-versa, when discharging and charging, respectively, electrons flow thru the long-circuit cations flow thru the electrolyte layer (WHITTINGHAM, YOSHINO, 2019). The charging procedure consists of electrons drive to the positive electrode resulting in oxidation and on the negative side being reduced (EROL, 2015).

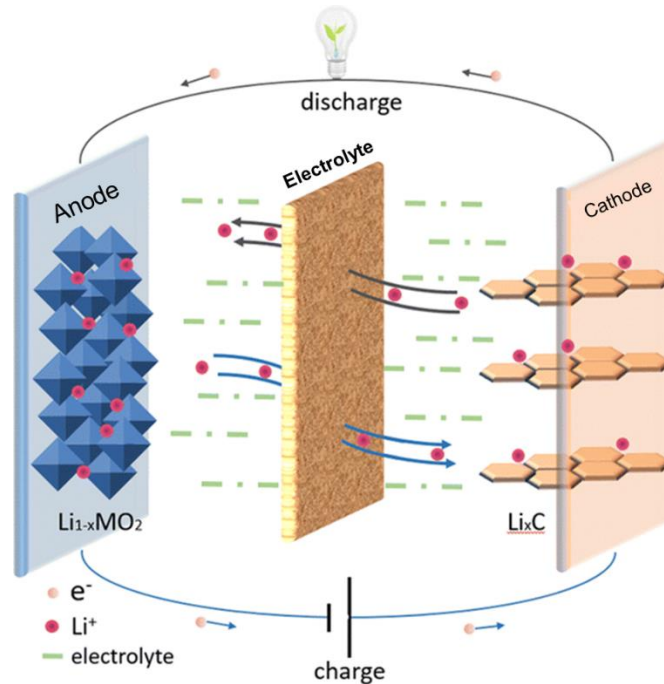


Figure 4-17: Schematic illustration of the electrochemical process in a lithium-ion battery.
Source: Adapted from SHENG, TONG, HE & YANG, (2017).

There is a variety of batteries in the market today, however, four (4) types of rechargeable are common, such as, lithium-ion (52%), nickel-cadmium (17%, NiCd), lithium polymer (4%) and nickel metal hydride (2%, NiMH), from which the lithium-base batteries deliver the most storage capacity per unit of space (3.7 V) that represents three (3) times the capacity of the nickel-cadmium or the nickel metal hydride batteries (GARRETT, 2004). These claims are followed by BUCHMANN (2019) and can be depicted in the figure below.

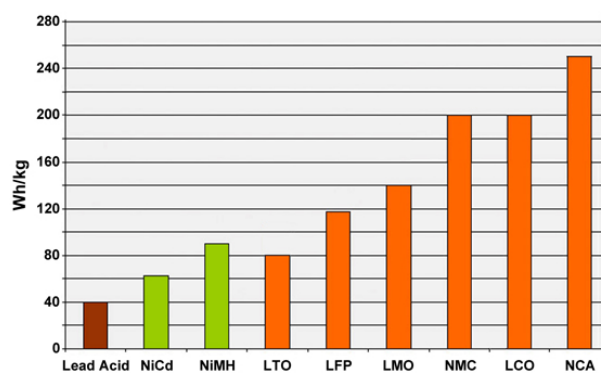


Figure 4-18: Typical specific energy of lead-, nickel- and lithium-based batteries.
Source: BUCHMANN, (2019).

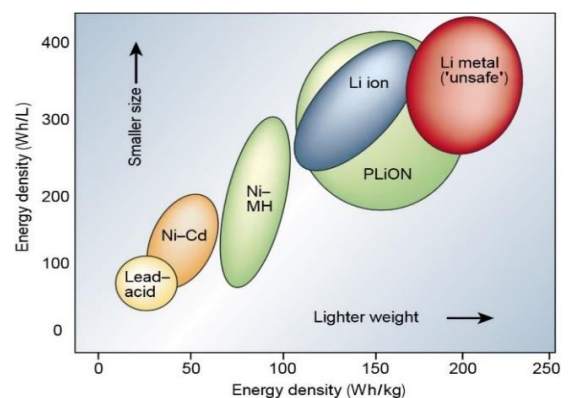


Figure 4-19: Comparison of energy densities and specific energy of different rechargeable batteries.
Source: DENG, (2015).

1.2.3.1 LIBs classification

LIBs can be composed from anodes of a graphitic carbon with lithium layered material with a copper current collector or lithium titanate (LTO) with a lithium-base metallic oxide cathode with a diverse composition type (DAHN, EHRLINCH, 2011) that are summarized in Table 4-2.

Table 4-2: Common positive electrode materials.

Material	Chemical formula	Abbreviation	Description
Lithium cobalt oxide	LiCoO_2	LCO	Original commercial type; expensive raw materials.
Nickel cobalt aluminium	$\text{Li}(\text{NiCoAl})\text{O}_2$	NCA	Highest energy density per unit mass.
Nickel manganese cobalt	$\text{Li}(\text{NiMnCo})\text{O}_2$	NMC NCM	Safer and less expensive than LCO, good cycle life and with promising technology.
Lithium manganese oxide	LiMn_2O_4	LMO	Safer and less expensive than LCO, but poor cycle life
Lithium iron phosphate	LiFePO_4	LFP	Very safe, high power, but lower energy density. Best high-temperature stability

Source: Adapted from LIGHTING GLOBAL, (2019).

A summarized comparison of the rechargeable batteries can be showed in the Table 4-3, where presents some key features such as the higher nominal voltage of the LIBs compared to others, non-toxic metals, higher LCA, lower self-discharge capacity per month, as well as working temperature conditions.

Table 4-3: Comparison of Li-ion (graphite anode) to other rechargeable battery chemistries.

Characteristic	LCO	LFP	SLA	NiCd	NiMH
Nominal voltage per cell	3.7	2.5–3.6	2.0	1.2	1.2
Specific energy (Wh/kg)	175-200	60-110	30-40	35-80	55-110
Energy density (Wh/L)	400-640	125-250	50-90	100-150	160-420
Cycle life (to 80% original capacity at 100% DOD ²)	500+	1000+	200-300 ³	300-1000	500-1000
Calendar life (years)	>5	>5	2-8	5-7	5-10
Ambient temperature during charge (°C)	0-45	0-45	-40-50	0-40	0-40
Ambient temperature during discharge (°C)	-20-60	-30-60	-40-60	-20-70	-20-65
Self-discharge capacity loss per month	2-10%	2-10%	4-8%	15-20%	15-30% (conv.) 2% (advanced)
Memory effect	No	No	No	Yes	Yes, less than NiCd
Toxic metals	None	None	Lead	Cadmium	None
Battery management sys- tem required	Yes	Yes	No	No	No

Source: LIGHTING GLOBAL, (2019).

Moreover, DAHN and EHRLINCH, (2011) expose some advantages and disadvantages in the use of LIBs showed in next table.

² **DOD** – Depth of discharge cycle.

³ Up to 400 at 80% DOD.

Table 4-4: Advantages and disadvantages of LIBs.

Advantages	Disadvantages
Sealed cells, no maintenance required	Moderate initial cost
Long cycle life	Degrades at high temperature
Broad temperature range of operation	Need for protective circuitry
Long shelf life	Capacity loss and potential for thermal runaway when overcharged
Low self-discharge rate	Possible venting and possible thermal runaway when crushed
Rapid charge capability	May become unsafe if rapidly charged at low temperatures ($< 0^{\circ}\text{C}$)
High-rate and high-power discharge capability	
High coulombic and energy efficiency	
High specific energy and energy density	
No memory effect	
Many possible chemistries offer design flexibility	
Can be made in aluminized plastic cases as “pouch” or polymer cells	

Source: DAHN, EHRLINCH, (2011).

1.2.3.2 New and future batteries

Despite lithium concentrates and LIBs market being on the rise, there are equally new batteries on development classified as “next-generation beyond LIBs” by TIAN, *et al.*, (2021), namely, potassium-ion (K-ion or KIBs) batteries, sodium-ion (Na-ion or NIBS) batteries, as well as all-solid-state batteries (ASSB or SSB) and multivalent (MV) batteries. TIAN, *et al.*, explains that these (K-ion and Na-ion) new technologies can become potentially more resourceful due to several elements such as cost-effective, high gravimetric and volumetric energy density, and raw material expenses make these new highly vital.

When evaluating the performance of LIBs, KIBs and NIBs, Libs hold a high relevance special related to its greater specific energy that is the double of the NIBs and KIBs, however, the cost of raw material can go from 3 to 15 times greater.

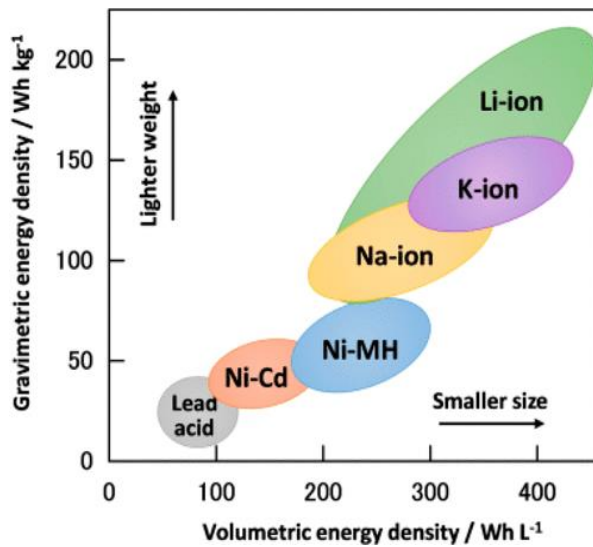


Figure 4-20: Gravimetric and volumetric energy density of different energy storage systems.
Source: ANOOPKUMAR; JOHN; TD, (2020).

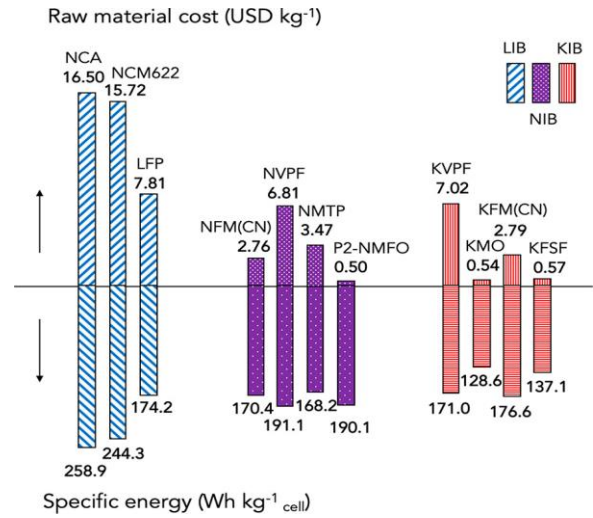


Figure 4-21: Cost of raw materials (upwards) and specific energy (downwards) for LIBs, NIBs and KIBs.
Source: TIAN, et al., (2021).

Ongoing research, presented by TIAN, *et al.*, (2021), suggest that rising SSB and new magnesium-ion batteries (MIBs) show a promising approach for EV and HEV industries.

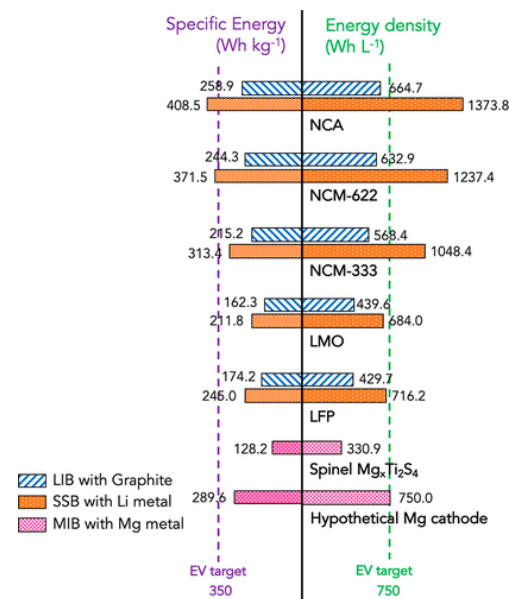


Figure 4-22: Specific energy and energy density of LIBs, ASSBs and MIBs with specific cathode materials, with the EV industry target.
Source: TIAN, et al., (2021).

When comparing the lithium, sodium and potassium, in terms of abundance, redox potential and market prices it is shown (Table 4-5) that there is abundance of sodium and potassium, evenly distributed globally when compared to lithium, however, the two have lower redox potential in aqueous medium, and lithium has the highest theoretical capacity of graphite. In the

other hand when, comparing market price for metric ton, lithium can be ten (10) times the prices for sodium and four (4) times potassium prices.

Table 4-5: Comparison between lithium, sodium and potassium.

	Lithium	Sodium	Potassium
Abundance in Earth's crust (wt.%)	~0.0017	~2.4	~2.09
Redox potential (V) vs SHE in aqueous medium	-3.04	-2.71	-2.93
Redox potential (V) in Propylene carbonate	-2.79	-2.56	-2.88
Theoretical capacity of graphite (mAh/g)	372	111.7	279
Geographical distribution of mineral resources	Majority of resources restricted to South America	Even distribution around the globe	Even distribution around the globe
Price/(metric ton of carbonate salts) (\$)	2,000-2,200	200-250	500-1,500

Source: JHON, TD, (2020).

Other emerging batteries are also coming to the market. Recently a partnership of CBMM, Toshiba and Volkswagen Truck & Bus launched a new e-Bus with lithium-niobium batteries with about 30 kWh usable capacity for each of the four battery packs (Valor International, 2024; Volkswagen Caminhões e Ônibus - Press Room, 2024).

1.2.4 Ore Processing

As previously described, lithium concentrates can be extracted from two main sources as noted, by brines and by hard rock granitic pegmatites. In this chapter both processing methods will be discussed and compared.

1.2.4.1 Brines

The concentration of lithium brines is a straightforward process that utilizes solar energy to create lithium carbonate through solar evaporation, solvent extraction, and precipitations to increase the lithium content. Initially, low-grade lithium deposits (0.05–0.15% Li) are found with high levels of competing ions and limited reactivity. The brines can be pumped from the deposit in a soluble form, mixed with clay, sand, and other mineral-rich salt crusts containing elements such as magnesium, sodium, potassium, iodine, and boron. The brines then evaporate and form halite (NaCl) and lithium chloride ions, along with other concentrates, through crystallization. Once the brine has reached a high enough concentration of lithium, the brine is then processed to extract the lithium using a solvent extraction process. The extracted solution is then treated with a precipitation process to purify the lithium into lithium carbonate, which is the final product. This process of lithium brine concentration is simple, efficient and environmentally

friendly, making it a popular method for producing lithium carbonate. (YOUNG, 2019; BRAGA, SAMPAIO, 2008).

Afterwards, NaCl is extracted from the pool followed by the solvent extraction of boron remaining over 1% Li from the brines. Furthermore, limestone is added which helps with the continuous evaporation and precipitation of Na and Ca to an extent that increases the degree of concentration to 38% LiCl or 6 %wt. Li, associated with 1.8% Mg and 0.8% B (BRAGA; SAMPAIO, 2008).

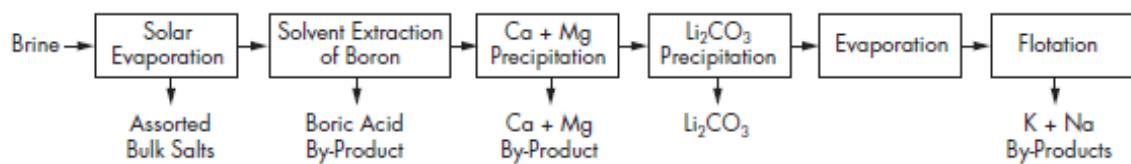


Figure 4-23: Lithium carbonate production flowsheet from lithium-brine.

Source: YOUNG, (2019).

Moreover, the crystallization and removal of magnesium and calcium hydroxides. At the end of the process, lithium carbonate (Li_2CO_3) is produced and sent to the concentration and processing plant (YOUNG, 2019; BRAGA; SAMPAIO, 2008). The steps explained can vary from one plant to another but in general the production of lithium from brines follows the similar as shown in Figure 4-23 and Figure 4-24.

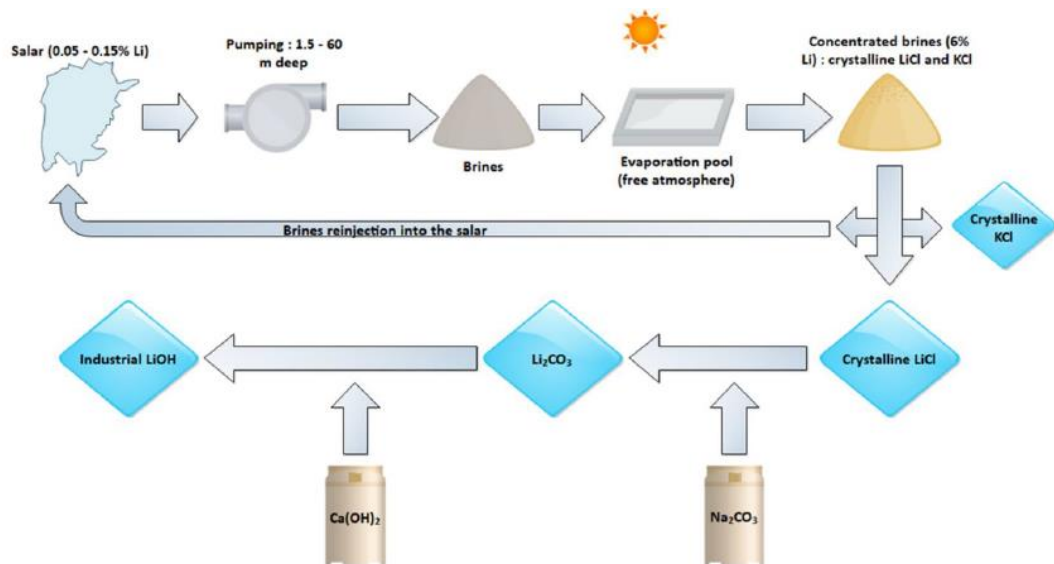


Figure 4-24: Lithium carbonate and lithium hydroxide production flowsheet from lithium-brine.

Sources: DESSEMOND, et al., (2019).

The lithium brines deposit grades can vary for each salar⁴ as low as 0.01% Li and as high as 0.31% Li as well as the ratio between Mg/Li (shown in

Table 4-6) that can precipitate and form undesirable crystallization such as $\text{LiCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (SCHMIDT et al., 2019), the Mg/Li ratio is important as it is the guiding factor for the dosage of limestone, if the ratio increases the grade of limestone also increases (SANTOS *et al.*, 2020). Altogether, depending on the zone the Li concentration can vary being the peripheral zones with the lowest grade of Li to the centre zone with the highest concentration (SANTOS *et al.*, 2020).

Table 4-6: Lithium-bearing brine deposits and their compositions (wt.%).

Brine	Li	K	Mg	Ca	B	Na	Cl	Mg/Li
Clayton Valley, USA	0.02 - 0.04	0.53 - 1.00	0.03 - 0.06	0.02 - 0.05	0.00 - 0.01	6.20 - 7.50	10.10 - 11.70	1.5
Salar de Atacama, Chile	0.11 - 0.31	1.80 - 2.97	0.82 - 1.53	0.02 - 0.04	0.06 - 0.07	1.03 - 9.10	2.03 - 19.85	7.5
Salar de Hombre Muerto, Argentina	0.05 - 0.06	0.52 - 0.62	0.05 - 0.09	0.05 - 0.099	0.02 - 0.04	9.79 - 10.30	15.80 - 16.80	1.5
Salar de Ricon, Argentina	0.03	0.62 - 0.66	0.28 - 0.30	0.04 - 0.06	0.04	9.46 - 9.79	15.80 - 16.80	10
Zhabuye Salt Lake, China	0.05 - 0.10	2.64 - 3.83	0 - 0.001	0 - 0.001	0.29 - 1.46	10.66 - 10.81	12.16 - 12.31	0.02
Qaidam Basin Salt Lake, China	0.01 - 0.03	0.60 - 0.66	0.47 - 3.51	0.02 - 0.42	0.03 - 0.05	6.20 - 6.84	9.20 - 20.42	117

Source: Adapted from SCHMIDT et al., (2019).

1.2.4.2 Hard Rock Pegmatites

Lithium-bearing minerals can be found in granitic pegmatites and the coarse size can vary depending on the orogeny of the rock. The latter will directly impact on the selection of processing method and equipment.

⁴ **Salar** – A term used in Southwestern United States and in the Chilean nitrate fields for a salt flat or for a salt-encrusted depression that may represent the basin of a salt lake ('salar', 2014).

Table 4-7: Specific gravity of different minerals present in granitic pegmatite rocks.

Mineral	SG (g/cm ³)	Mineral	SG (g/cm ³)
Spodumene	3.10 – 3.20	Quartz	2.65
Feldspar	2.55 – 2.76	Mica	2.80 – 3.40
Petalite	2.40	Zinnwaldite	2.90 – 3.10
Lepidolite	2.80 – 3.00	Columbite-Tantalite	6.30 – 8.20
Muscovite	2.77 – 2.88	Cassiterite	6.98 – 7.01

Source: Adapted from YOUNG, (2019).

Physical separation of lithium minerals is liberated in large coarse size (>1 – 2 mm) than methods focused on specific gravity (SG) or density can be used, since ore-minerals and gangue can have significant SG's as shown in Table 4-7. For a long time, due to the diverse density found in pegmatite minerals the use of spirals was considerably relevant and widely implemented for many the separation of denser mineral such as cassiterite and columbite-tantalite, as depicted in the plant example in Figure 4-25. However, the use of dense medium separation (DMS) by gravity separation using cyclones can be used to separate spodumene with feed size as low as 0.5 mm and greater than 2 mm which present a more capable separation (YOUNG, 2019). According to TADESSE *et al.*, (2019), in the case of Bald Hill coarse particles with -12+1 mm are separated into two distinct sizes, first a coarser fraction and a middling fraction, with -12+5 mm and -5+1mm, respectively, whereas both fractions are processed in two stages (rougher and cleaner) by DMS cyclones and producing spodumene concentrates from the underflow secondary cyclones.

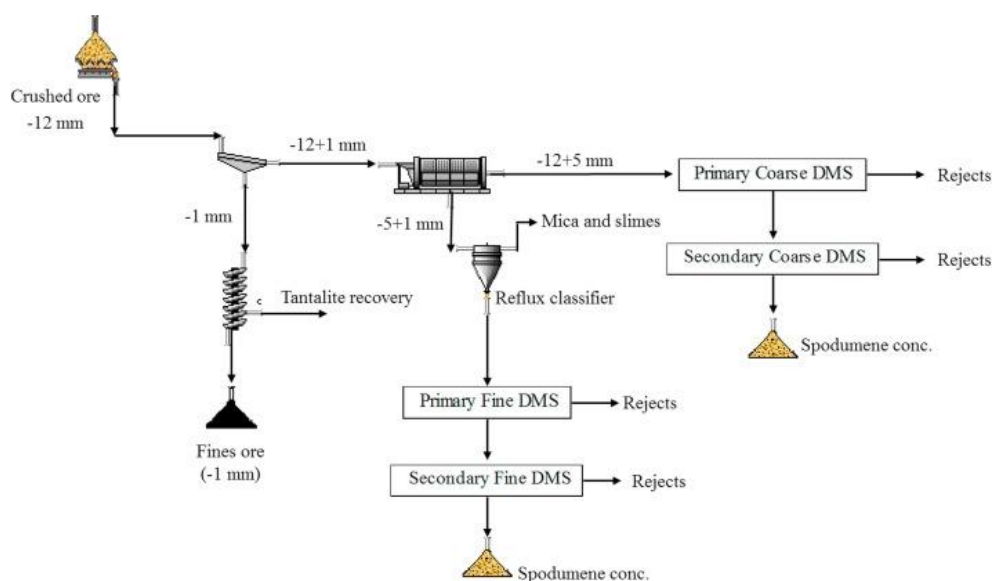


Figure 4-25: Example of a simplified tantalite spiral concentration and spodumene DMS concentration from Bald Hill plant.

Source: TADESSE *et al.*, (2019).

Hence, for more fine particles the need of more specific concentration methods is required. Flotation cells have been used for the concentration of particles with P_{80} of 106 μm product of ball mill (with a F_{80} of 0.5mm) in a closed circuit with desliming cyclones, depicted in Figure 4-26. Moreover, direct flotation is done in three stages, one rougher stage and two cleaning stages (cleaner and recleaner) to obtain a 6.0% of Li_2O .

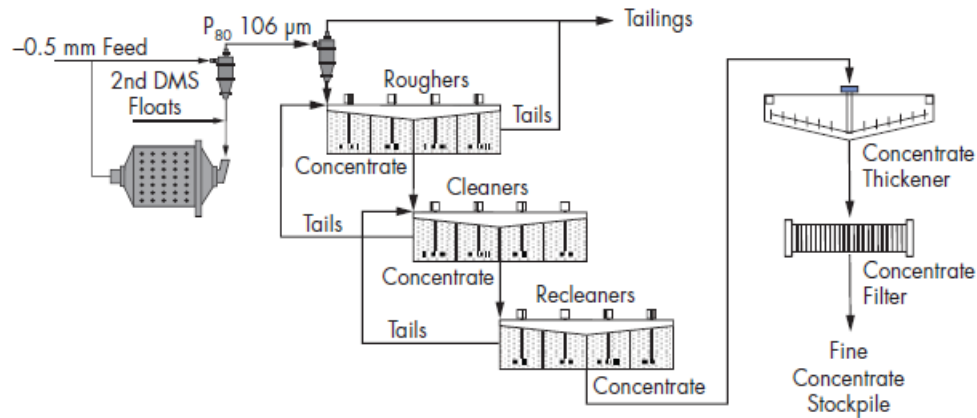


Figure 4-26: Spodumene flotation flowsheet, with 6.0 % Li_2O concentrate.
Source: YOUNG et al., 2019.

Since spodumene in DOL of spodumene is found in more coarse size range in the Brazilian Lithium Company (Companhia Brasileira de Lítio, *in Portuguese*), CBL, the dressing plant of lithiferous pegmatite of the Cachoeira underground mine, with a dept of 180m and 5 km long, consist of crushing and sieving, followed by a DMS concentration to produce a 5.5% Li_2O spodumene concentrate and capacity of 30,000 tpa.

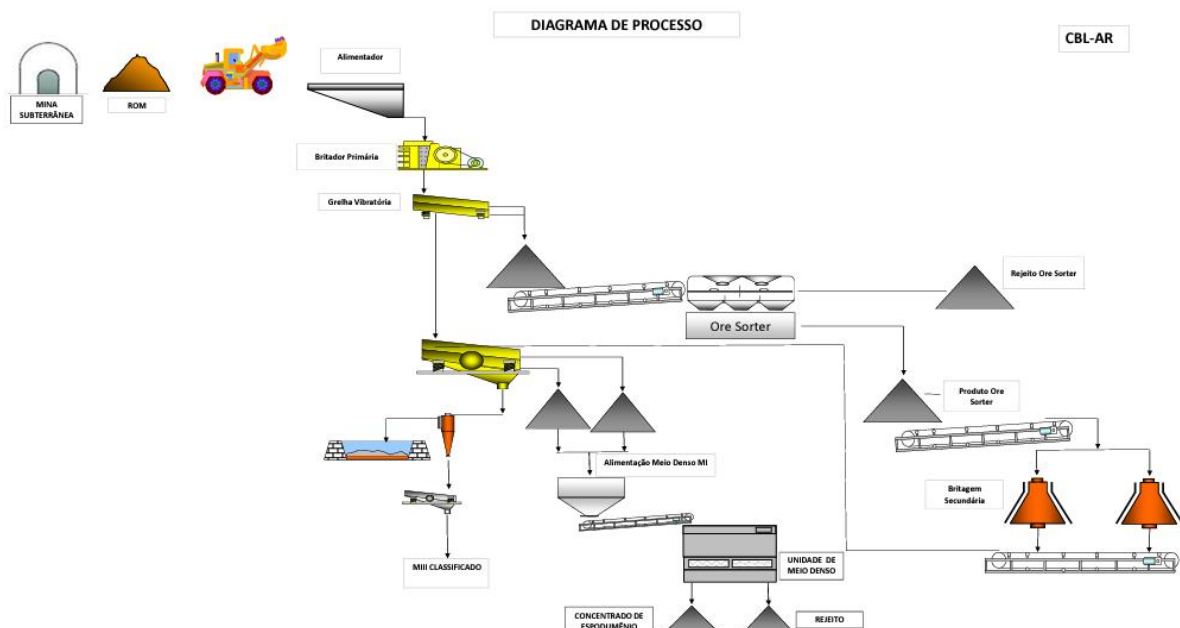


Figure 4-27: CBL spodumene process flow-sheet diagram, with 5.5% Li_2O concentrate.
Source: CBL.

On the other hand, AMG Brazil – Mineração dressing plant consists of a regulation tank followed by a sieving in closed circuit with a ball mill, afterwards a desliming cyclone and magnetic separator both tailings (slime and magnetic particles, respectively) are directed to tailings dam 3. The concentrate is directed to a thickener before spodumene flotation concentration. The tailings that contain mainly aluminosilicates are sent to the sodic feldspar plant and the spodumene concentrate after thickening are dried and stocked with an average of 5.5% Li_2O content and production of 30 ktpa with a plant design feed of 90 ktpa (plant I) (SOARES, 2021) and targeting capacity expansion for 130 ktpa (AMG, 2022).

nevertheless, Fe_2O_3 in this size has a recovery above 65.0% and 0.5% grade, that states a severe problem. In the other hand, 74 μm and under present good Li_2O grade and recovery, with 5.8% and 76.8%, respectively, but always followed by Fe_2O_3 associations 0.6% and 75.8%, grade and recovery, respectively.

Furthermore, SOARES (2021) shows that when comparing bench and industrial tests there are significant differences, for flotation greater than 149 μm there is a gap of close to 30% recovery, with 56.9% and 28.1% for bench and industrial tests, respectively, with non-significant change in the iron oxide content. However, when analysing the 149 μm sizing there is shown a lower range of 15% recovery, with 71.2% and 56.4% for bench and industrial tests, respectively, but the iron oxide does not follow the same behaviour, it decreases with the lower sizing, with close to 15% recovery gape, with 29.2% and 43.4% for bench and industrial tests. This can be related to the drag force in the industrial stage. Further testing should be held to understand this behaviour.

1.3 FROTH FLOTATION

1.3.1 General Aspects of Froth Flotation

There are vast techniques that seek an efficient, selective and monomineralic separation for mineral concentration. PEREZ, *et al.* (2007) defines concentration as steps by which there is a separation of mineral species depending on the final usage, using mineral differential proprieties such as colour, magnetic susceptibility, density, surface charge, hydrophobicity (WILLS; FINCH, 2016), or particle size etc. Separation techniques can be classified as:

- Gravity or dense methods.
- Magnetic methods.
- Electrostatic methods.
- Froth flotation.
- Others.

However, these methods have some certain limitations in special for particle size range, shown in Figure 4-29, gravitational, dense, and electrostatic methods are more restrained for more coarse particles, whereas magnetic and flotation methods can reach lower 1 μm . Moreover, the magnetic only applies for susceptible mineral and, on the other hand, froth flotation can be applied by most of the minerals by inducing hydrophobic or hydrophilic proprieties on the mineral surface charge.

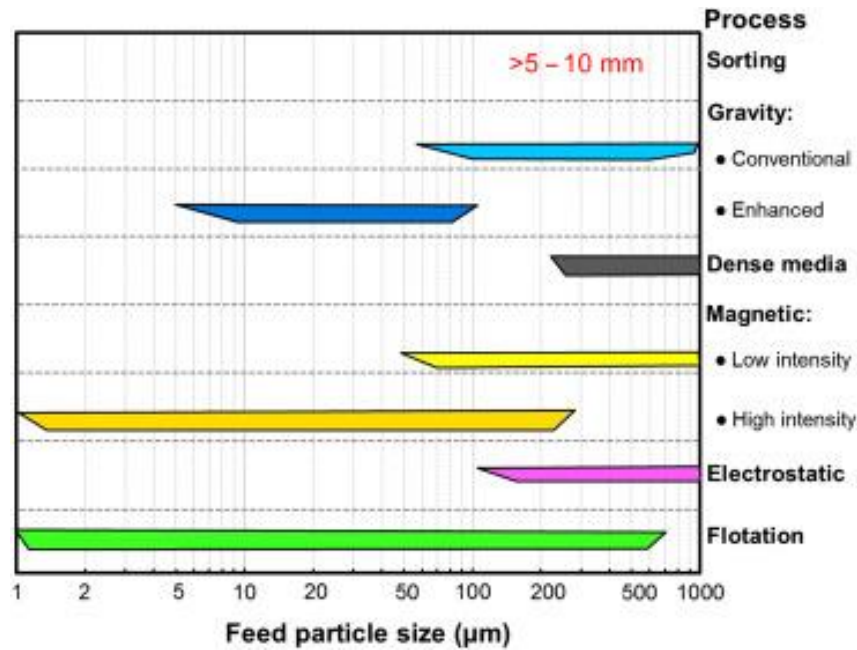


Figure 4-29: Effective range of application of selected mineral separation techniques.
Source: WILLS; FINCH, (2016).

KAWATRA (2011) defines froth flotation as a multifaceted method that uses a veracity of physical phenomenon's, such as hydrophobicity and hydrophilicity, adhesion, and repulsion to polar and/or non-polar surface, to achieve particles separation in a mineral-water slurry by adhesion to air bubbles. It consists of phases interactions of the three phases of the matter (liquid, air and solid) with a chemical treatment to the mineral surface by surfactants that adsorb in the active sites, these surfactants can be collectors, depressants, activators, and other modifiers, and frothers for reduction of surface tension.

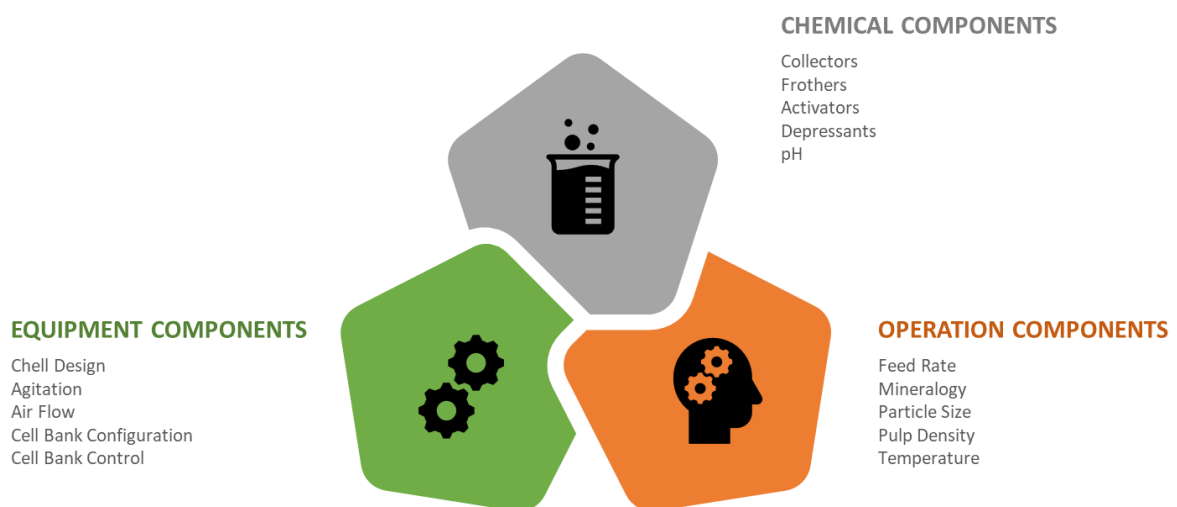


Figure 4-30: Froth flotation system interrelated components.
Source: Adapted from KAWATRA, (2011), apud Klimpel, (1995).

Froth flotation consists of three basic conditions, namely:

- **Releasability or liberation** – related to the particle's association or dissociation of one or more mineral species and the DOL, regarding the fragmentation and classification previous phases.
- **Dynamic separation** – related to the flotation machine-derived factor functionality such as bubble diameter and particle size, air rate, rheology of the slurry, etc.
- **Differentiability** – related to the ability of monomineralic separation by inducing superficial proprieties such as hydrophobicity or hydrophilicity, bubble-particles aggregation, capacity of resisting the water thrust and breaking the water superficial tension.

The last condition is directly related for the wetting of surface of the mineral and later attachment to the bubble. This propriety is associated to the mineral composition and surface structure, which can be altering the surface conditions by adding surfactants with polar hydrophilic head and non-polar hydrophobic body/tail.

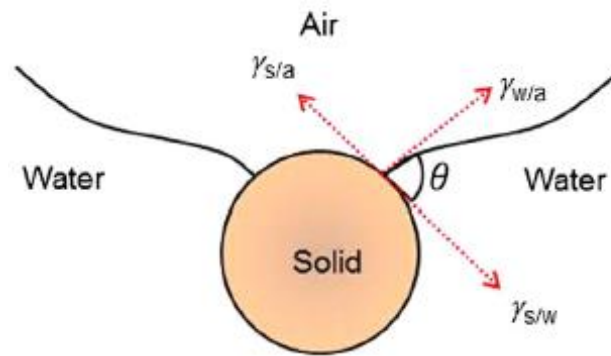


Figure 4-31: Particle attached to a bubble and the solid-water-air phase interaction.

The interaction of these three phases indicates the ability of a particle to be hydrophobic or hydrophilic, depending on the contact angle. The air-solid-water interface describes the wettability of a particle that is directly related to the hydrophobicity of the solid, in this case, mineral particles can be determined by measuring the three-interface contact angle (θ), measured by the surface tensions or energies between the solid-air ($\gamma_{s/a}$), solid-water ($\gamma_{s/w}$) and water-air ($\gamma_{w/a}$) interface tensions:

$$\gamma_{s/a} = \gamma_{s/w} + \gamma_{w/a} \cos \theta \quad (1)$$

Whereas the specific energy can be determined from the *work of adhesion* ($W_{s/a}$) of the solid air that can be calculated using equation:

$$W_{s/a} = \gamma_{w/a} + \gamma_{s/w} - \gamma_{s/a} \quad (2)$$

And combining the (1) and (2):

$$W_{s/a} = \gamma_{w/a}(1 - \cos \theta) \quad (3)$$

This can depict as shown in the figure below, where the contact angle is measure in the solid-water interface:

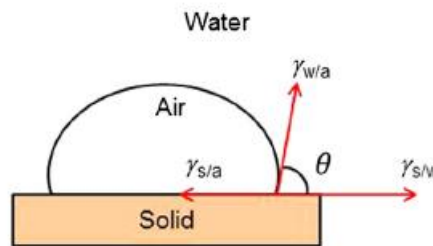


Figure 4-32: Three-phase contact angle and surface tension forces.

The wetting of the mineral particles generates surface charges that is the outmost condition for the reactions such as adhesion, dissolution, oxidation, and other acid-base reaction (BALTAR, 2021) and surface zeta potential. Where the latter, is used to determine the surface energy on the electric double layer (EDL), that forms the Stern cloud, that is characterized internally by the Inner Helmholtz Plane (IHP or surface potential) and Outer Helmholtz Plane (OHP or Stern potential) and externally by the diffused layer (PEREZ, *et al.*, 2007).

In the between the positive (cations) and negative (anions) ions, there are water molecules that interact with the ion's adsorption alongside their counter-ions, as shown in Figure 4-35, in the case of oxygen with cations (red box) and hydrogen with anions (blue box). The negatively charged solid surface leaves gaps for cationic surfactant adsorption, or somewhat amphoteric surfactants that have both positive and negative heads.

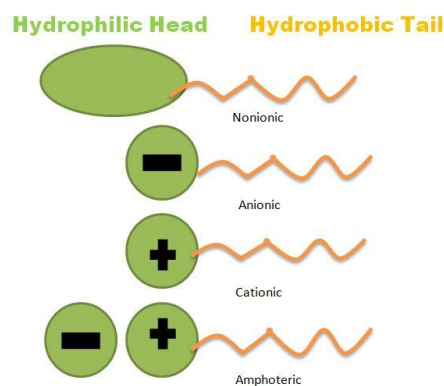


Figure 4-33: Surfactants types and their head charge.

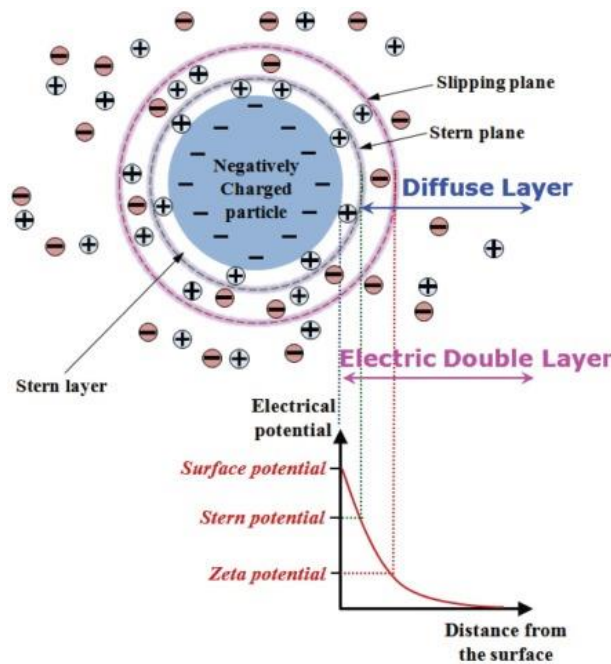


Figure 4-34: Schematics of the EDL with specific electrical potential zones.
Source: PARK, SEO, (2011).

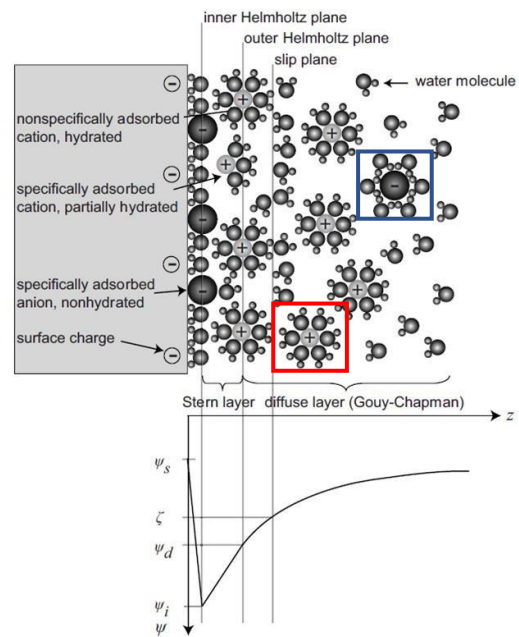


Figure 4-35: Schematic representation of the EDL and the corresponding potential profile.
Source: MA, (2019).

The zeta potential (ψ_ζ) measures can vary alongside the hydrogenionic potential (pH), as shown in Figure 4-36, where the point of zero charge (PZC) is presented for minerals such as spodumene, microcline, quartz and muscovite, at pH of 3.0, 1.8, 2.5 and 2.8, respectively (VIANA, 2006).

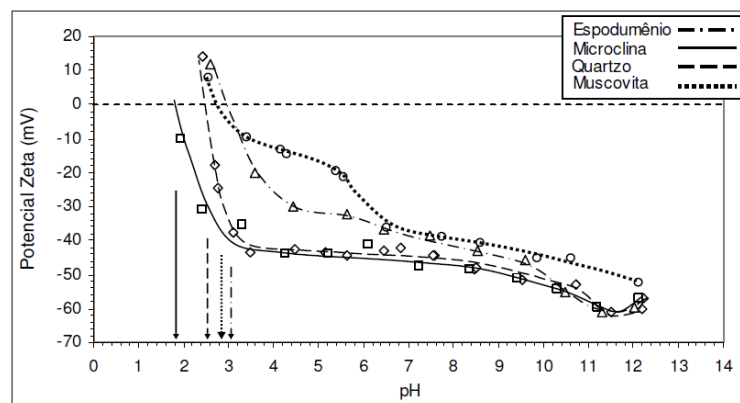


Figure 4-36: Zeta potential of different pegmatitic mineral alongside various pH range.
Source: VIANA, (2006).

Collectors can be classified in accordance with by their polar ionization (anionic or cationic) and their application (for non-sulphides or sulphides). The anionic are subdivided into *sulphydryl* with R-SH bonds and they can be xanthates, dithiophosphates and dithiocarbamates, and *oxyhydriyl* that have R-OH bonds they can be carboxyls, sulphates and sulphonates. The cationic collector can be divided into amine with one R radical and amine ethers with larger hydrocarbon

adding Ca^{2+} ions (120 mg/L) to flotation of spodumene with collector NaOL (250 mg/L) can expand the floatability from 60% to over 90% for 40-80 μm particles in a neutral pH.

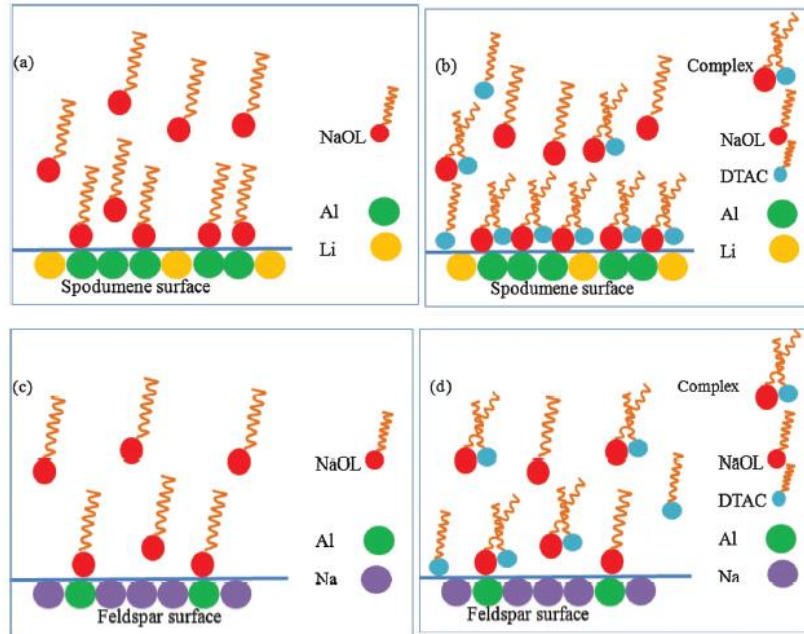


Figure 4-38: Surfactant adsorption of NaOL on spodumene (a) and feldspar (c) surfaces and NaOL/DTAC collector on spodumene (b) and feldspar (d) surface.

Source: XIE et al., (2020).

Table 4-8: Essential results and conclusions of the flotation of spodumene collectors.

Collectors	Main results and conclusions
Single collectors	
DDA, NaOL, BHA	Flotation behaviour or selectivity is usually poor. It mainly utilized in the basic research.
Mixed collectors	
NaOL/DTAC	Mixed minerals (2.62% Li ₂ O) flotation test: Li ₂ O grade: 5.57%; recovery: 71.13%. The collector consumption decreased compared with the original plant setup. Mechanism: NaOL/DTAC showed higher activity and denser molecular arrangement.
NaOL/TTPC	There was synergistic effect of NaOL/DTAC in the water-air interface. Recovery (single mineral flotation test): spodumene (72%), feldspar (1%). Mixed minerals flotation test: Li ₂ O grade: 4.6%; recovery: 88%. Mechanism: The NaOL and TTPC were adsorbed on spodumene surface respectively through chemisorption and electrostatic attraction.
DDA/NaOL	Recovery (single mineral flotation test): spodumene (85%), feldspar and quartz (<20%). Mixed minerals (1.48% Li ₂ O) flotation test: Li ₂ O grade: 5.59%; recovery: 75.24%. Mechanism: DDA could obviously increase the adsorption of NaOL on spodumene (001)
HPA/DIDA	surface. The association of DDA ions and oleate was the most preferred. Recovery (single mineral flotation test): spodumene (85.61%), feldspar (7.38%). Mechanism: It adsorbed on spodumene surface by synergistic effect of chemisorption and hydrogen bonds adsorption, and it was adsorbed on feldspar surface only by chemisorption.
DDA/ oxidized paraffin sodium salt	Concentrate: Li ₂ O grade: 6.02%; recovery: 87.34%.
Supermolecular collectors	
DPA-BDDA	Recovery (single mineral flotation test): spodumene (82.14%), feldspar (32.48%) Mechanism: DPA-BDDA was adsorbed on spodumene surface through both electrostatic attraction and chemisorption, and it was adsorbed on feldspar mainly by electrostatic attraction.

Source: Adapted from XIE et al., (2020).

1.3.2 Flotation Equipment

SOUZA (2020) explains that prior flotation process there is a necessity of particle size reduction, separation, and conditioning before dressing processes. However, there are equipment's for coarse particles, some will be presented in this topic.

Before the start of the flotation processes, there is a previous conditioning of the slurry with the collectors, regulators and frothers (when needed), this step can be done in conditioning cells or on the slurry pipelines, this depends on the type and time of adsorption mechanism, and other key conditions such as solid percentage (% solid).

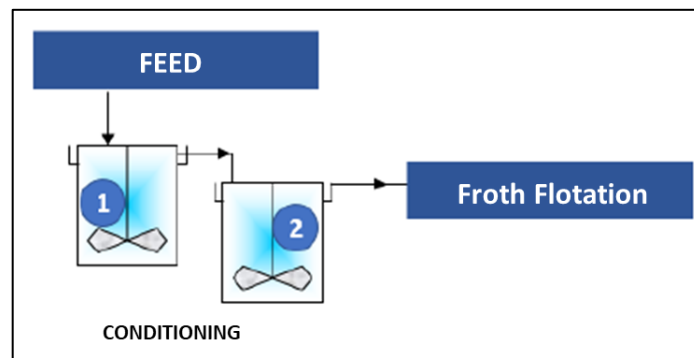


Figure 4-39: Conditioning cells and two stage flotation steps.
Source: Adapted from SOARES, (2021).

1.3.2.1 Mechanical cells

Widely applied in the mineral dressing industry, it consists of two specific parts a rotor that rotates with blades or impeller to agitate the slurry (ore-water mixture) and air injector in the middle of the rotor that sprays air bubbles all over the cell (WILLS; FINCH, 2015), as depicted in Figure 4-40.

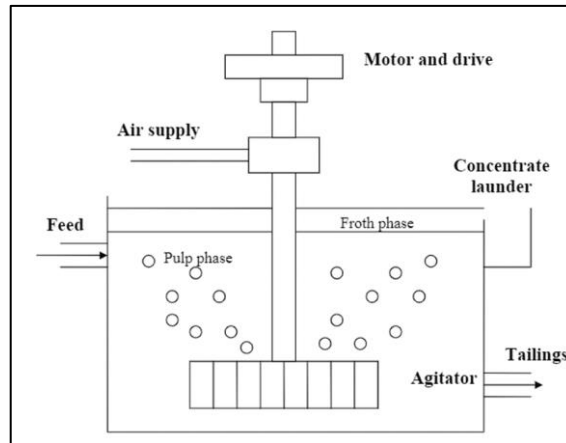


Figure 4-40: Mechanical flotation cell schematics.

It is noted that there are two phases in the mechanical cell, first the pulp phase and second the froth phase. The pulp phase consists of an area of collision between particles and air bubbles resulting in contact and attachment or repulsion, depending on the polar energy of the particle, afterwards the pair tends to raise by dense differentiability of the water and air bubbles which enter the froth phase that is mainly a foam formed carrying the collected particles but also some gangue carried by for mineral liberation due to DOL or entrainment of the gangue particles.

Furthermore, depending on the weight capacity of the bubbles this can collapse resulting in particle detachment, however, when there isn't air bubble collapse there is the washing of the air bubble. At the end at the froth recovery zone, the floated particles trapped in the foam are discharged from the cell and collected as final product or directed to further processes, the same goes for the tailings that are collected from the bottom of the cell and director.

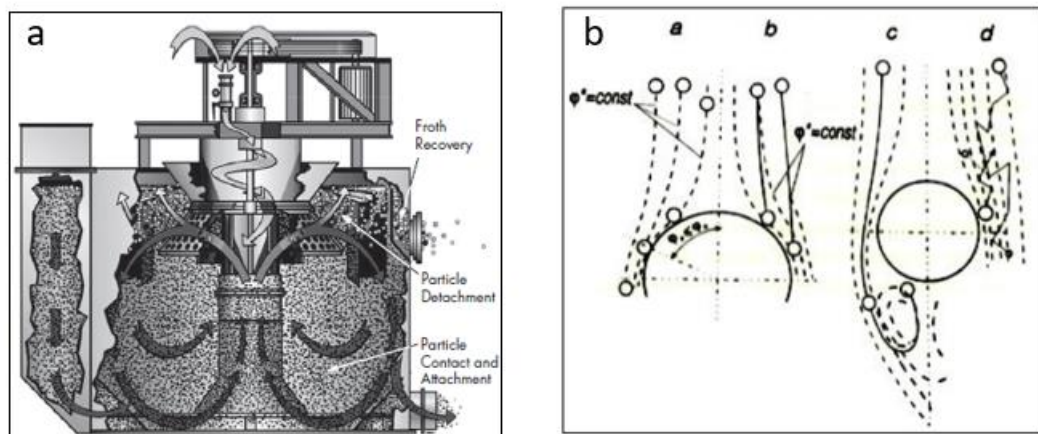


Figure 4-41: (a) Schematics of a WEMCO SmartCell with zone division and (b) particle collision and attachment mechanisms to air bubble.

The relative size of mechanical flotation cells has seen a growth over the years from as lower than 1 m^3 in the 1940's to close to $1,000 \text{ m}^3$ in 2020 (see Figure 4-42).

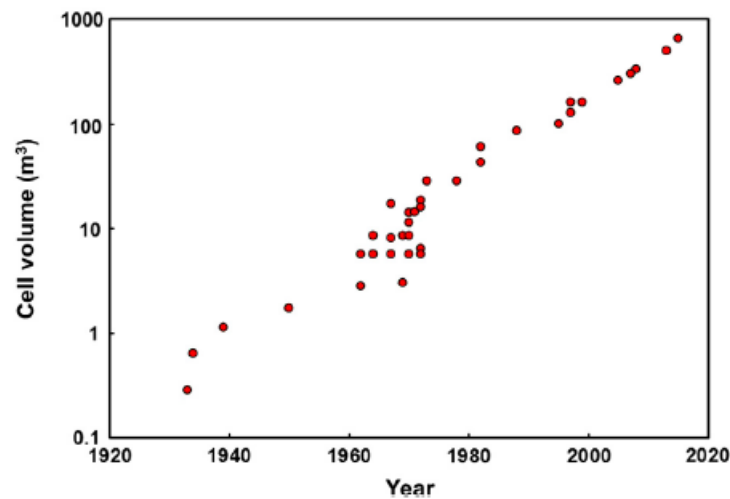


Figure 4-42: Trends of flotation cell volume over 100 years.
Source: WILLS, FINCH (2015).

1.3.2.2 Column flotation

YOUNG (2019) explains that different from the mechanical cell, the column flotation has a more stable rheological zone that reduces the agitation of the slurry and sub consequently the entrainment of gangue particles, making it possible for the flotation of finer particles, this differs to mechanical cells as in the presence of ultrafine particles there is a slime coating effect of the larger particles downgrading the selectivity and flotability of the cell. The column flotation (Figure 4-43 presents a solution to the contamination of the concentrate by “adding” a wash water to the process after collision and attachment to the bubbles. As the bubble flows upwards water particles flow downwards creating a current and it differs depending in which zone of the column it is whether in the gas holdup in the pulp (ϵ_p) zone with average of 10-20% by bubble volume, in the stabilized (ϵ_s) with over 60-70% of the bubble volume and >90% of the froth zone (ϵ_f) as shown in Figure 4-44. Commonly used at cleaner stage (SOUZA, 2020).

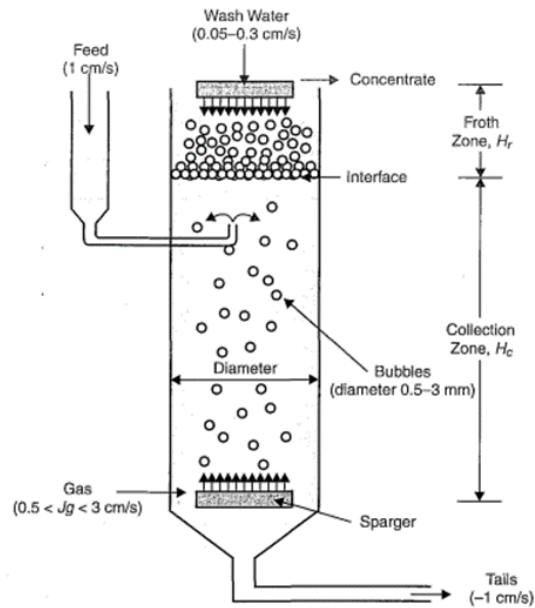


Figure 4-43: Schematics of column flotation for conventional flotation.

Source: SILVA, (2015) apud FUESTENAU AND HAN, (2003).

SILVA (2015) and SOUZA (2020), explains that the slurry is fed about one third of the top of the column and with air injection on the base of the column, shown in Figure 4-43, with the descendence of the pulp due to gravity and ascendance of the air bubbles due to relative density, respectively, they meet up in the collection zone (H_c), after collision and adhesion the collected particle both ascend to the froth zone (H_f) where it is washed to clean dragged fine particles.

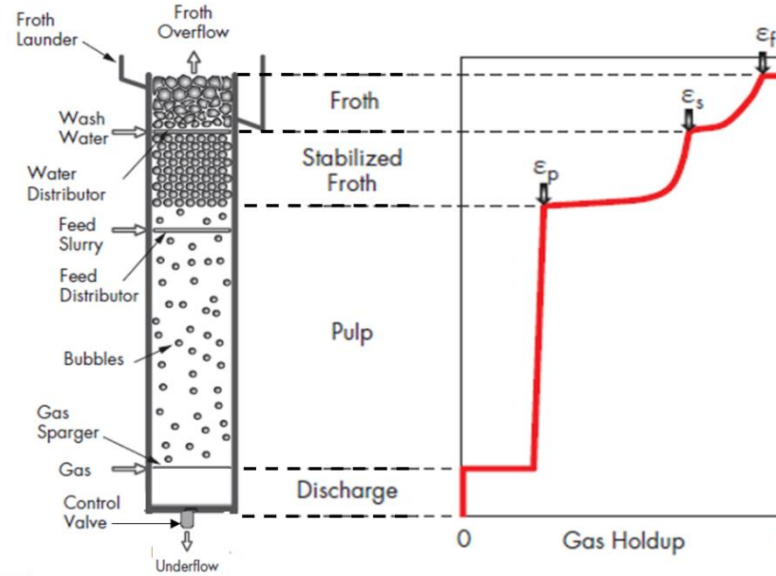


Figure 4-44: Schematics of the column flotation and the gas holdup in the pulp (ϵ_p), the stabilized (ϵ_s) and the foam (ϵ_f) zones.

Source: Adapted from YOUNG, (2019).

FUESTENAU AND HAN (2003) explain that industrial column has between 9 – 14 m in height and a diameter less than 2 m, the main operational conditions consist of the superficial velocities (J) with key controls for:

- Gas velocity (J_g) (0.5 – 3.5 cm/s).
- Pulp feed velocity (J_p) (0.7 – 2.0 cm/s);
- Wash water velocity (J_w) (0.1 – 0.8 cm/s) and.
- Bias water velocity (J_b) (0.07 – 0.3 cm/s).

1.3.2.3 Pneumatic flotation

Pneumatic cells (Figure 4-45) are more static equipment's with no mobile configurations that have gain notice for their rapid kinetics and lesser residence times when compared to mechanical and column cells and more compact equipment's, one of the biggest advantages of the use of the pneumatic cell is the ability to reduce entrainment when applying wash water. It consists of jet injection (high pressure or speed) of air and slurry from the top of the cell with froth washing water added on the top (YOUNG, 2019; SOUZA, 2020; SILVA, 2015; WILLS; FINCH, 2015).

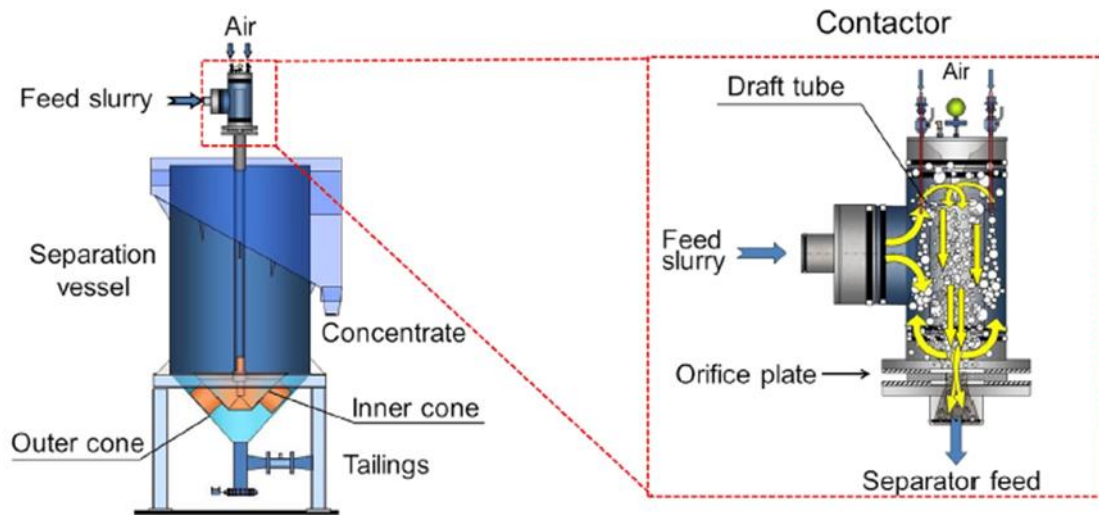


Figure 4-45: Schematics of a Contact cell and draft tube of air/pulp contact mechanism.
Source: WILLS, FINCH, (2015).

SILVA (2015) explains that to achieve an efficient flotation some probable interactions must be met, such as particle – bubble contact, adhesion, transport between slurry and froth and collection probability. The pneumatic cell enhances the particle – bubble contact interaction probability that has a consequence in bubble diameter (d_b), higher surface contact area and higher adhesion chances, making it more probable for flotation achievement when compared to the mechanical cell and column.

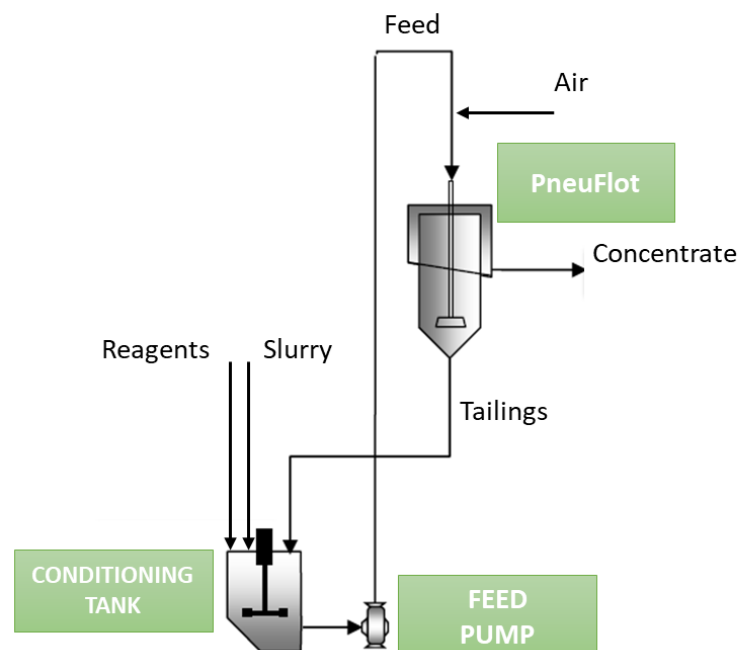


Figure 4-46: Schematics of pneumatic cell for entrainment test.
Source: Adapted from SILVA, (2015).

SILVA (2015), describes some of the main characteristics of the pneumatic flotation cell as for:

- Efficient recovery for fine and coarse particles, where conventional flotation is less efficient.
- Less installation space necessity due to shorter cell size.
- Less energy consumption due to no need of a rotor for slurry agitation.
- More stable rheology due to non-mobile parts.
- Capacity of coarse flotation when compared to conventional flotation.
- Larger granulometric size distribution of the pulp/slurry.
- Less residence times.

1.3.3 Flotation of Fine Particles

There is a growth of tailings dams that contain great amount of mass with low-grade mineral, however, with high DOL. FARROKHPAY, FILIPPOV and FORNASIERO, (2021), explain that low-grade deposits have become cost-effective and exploitable due to new technologies in fine particles processing. More on that note, they explain that the problem of recovery of fine particles is often related to the particle-bubble collision and on the contrary to coarse particles where the poor recovery is due to particle detachment from the air bubble in consequence of the high agitation in cell, related to the gravitational drag and low DOL. Moreover, SOMASUNDARAN (1980), discloses that reduced particle sizes as two dominant aspects being first the enlargement of the specific surface area (SSA) and the depression of particle mass as a result fine particle are often dragged to the froth by entrainment by the water at the external of the bubble or by entrapment within the floated particles. A consequence of the fine particles large SSA impacts the adsorption of the chemical reagent capacity. For this reason, processing of ore systems such as hematite and spodumene require a prior desliming.

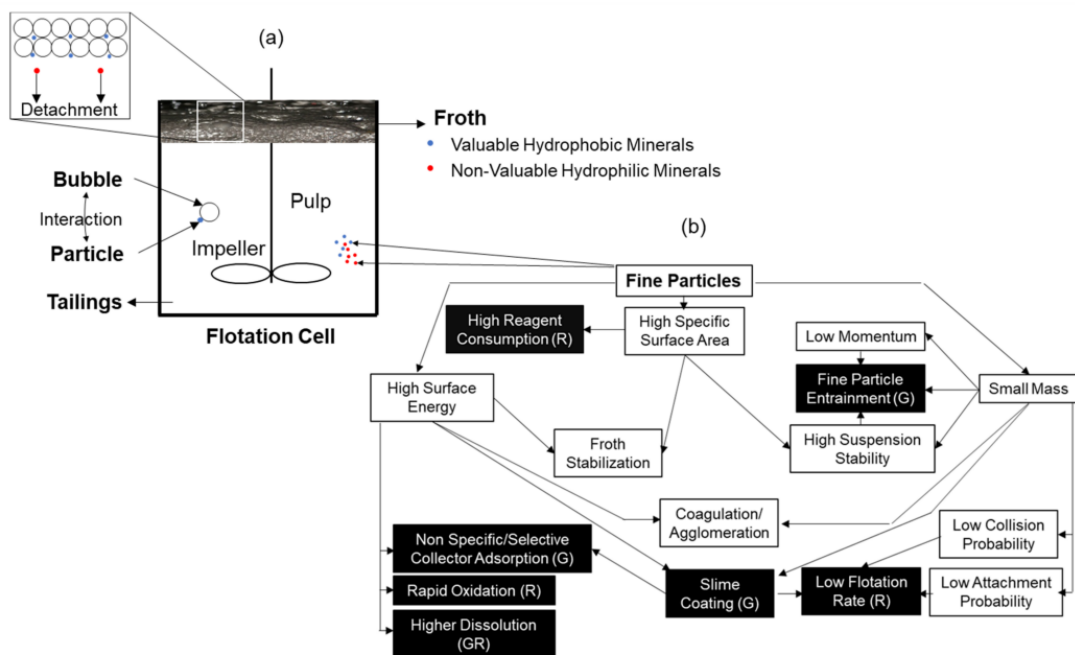


Figure 4-47: a) Schematic explaining the principle of a mechanical froth flotation process. b) Schematic diagram showing the relationship between physical and chemical properties of fine particles and their behaviours in

flotation; (G) and (R) refer to whether the phenomenon affects the grade or recovery, individually or both together. The highlighted (black) cells indicate the possible drawbacks of the presence of fine particles on flotation performance.

Source: SAJJAD, OTSUKI, (2022).

SOMASUNDARAN (1980) continues clarifying that the surface and electrochemical properties of the same material differ in-between fine and coarse particles. Some aluminosilicate mineral tends to liberate cations from the surface resulting in surface activation, depending on or the circumstances, resulting in unwanted activation of depression. As particles turn into finer particles observe higher SSA energy because of crystallographic imperfections, increased edges numbers and corners, thus colloidal particles trend to have enlarged range of intermolecular forces and EDL forces being the main influence and leading particle interaction between this and bubbles and other particles. When EDL is thick and the potentials are large, colloidal particles are usually very dispersed, however, when the EDL is thin or absent, there will be tendency of coagulation due to attractive forces, moreover, when the colloidal particles are hydrophobic these particles will adhere to air bubbles in the mixture. This agglomeration properties of the mineral colloidal particles have been studied and used as a method of coagulating and floating fine particles. Whereas, when these particles adhere to larger particles there is a process named *slime coating* where long-range intermolecular forces dominate the process of interaction and have a great consequence to the recovery of valuable minerals and coarse particles, lowering in grade of the concentrate significantly.

While evaluating the correlation between flotation and rheology of fine particles suspensions SAJJAD and OTSUKI (2022), observed that three main forces dominate the degree the rheology of suspended particles associated to the particle sizes, namely: hydrodynamic, Brownian and colloidal forced, for coarse to ultrafine particles (shown in Figure 4-48). The authors observed that, for coarse particle ($d_p > 10 \mu\text{m}$) are governed by hydrodynamic forces, for fine particles ($10^{-3} \mu\text{m} < d_p < 10 \mu\text{m}$) a combination of hydrodynamic and Brownian forces dominant the flow behaviour, whereas for ultrafine particles ($d_p < 10^{-3} \mu\text{m}$), Brownian and interparticle colloidal forces are shown to lead the rheology of the particles.

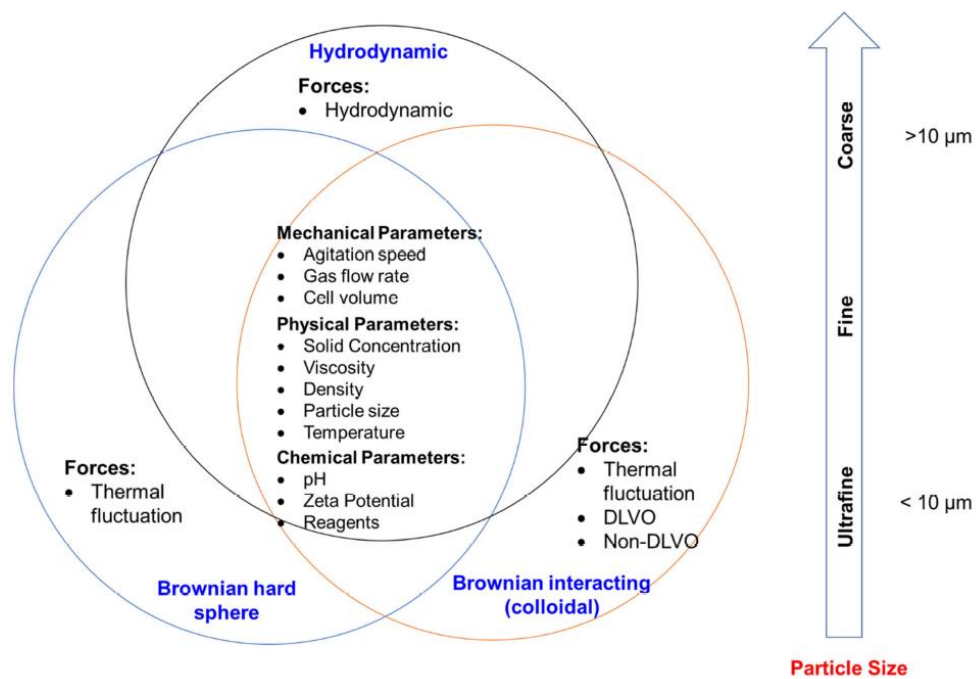


Figure 4-48: Particle size ranges and their associated flow regimes, forces and parameters influencing flotation performances.

Sources: SAJJAD, OTSUKI, (2022).

FARROKHPAY, FILIPPOV and FORNASIERO (2021), complement that low recovery of fine particles, when compared to coarse particles, is a result of different conditions for chemical and hydrodynamic conditions. In the case of finer particles, of higher SSA there is a larger amount of collector, rapid oxidation and high surface dissolution in the froth flotation process, and a consequence of the small mass there is a low momentum and high entrainment on colloidal particles on the bubble carried, thus, increasing the froth height and sub consequently the dynamic froth stability.

The entrainment process is carried out by fine particles ($d_p < 20 \mu\text{m}$) that are dragged along the up-rising bubbles in the Brownian state suspension particles in the slurry, resulting in the drag by non-adsorption on the air bubble leading to transportation of gangue materials to the floated.

To improve to the flotation process, more precise particle-bubble collision (P_c) and attachment (E_a), low turbulent, and with wash water cells are needed to enhance the flotation. Where the column and pneumatic cells have shown to reduce entrainment and improve fine particles separation, especially in the case of the column cell due to the wash water (FARROKHPAY, FILIPPOV and FORNASIERO, 2021).

1.4 MODELING AND OPTIMIZATION

1.4.1 Flotation Models

Froth flotation is divided in two categories, namely, micro-scale and macro-scale models associated to the flotation kinetics (GHARAI; VENUGOPAL, 2015). In the macro-scale the subdivision into more complex and detailed models as presented below:

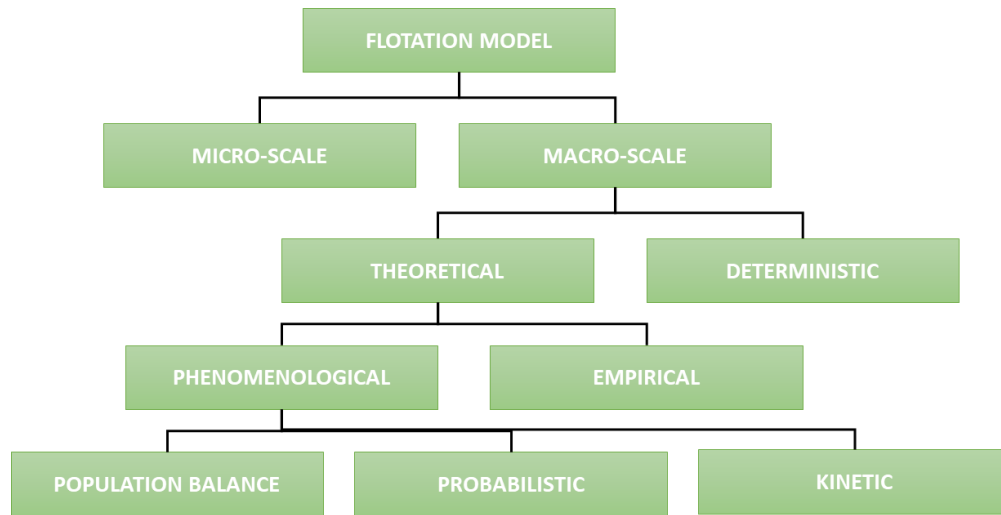


Figure 4-49: Flotation models' general classification based on overall processes and sub-processes occurring in flotation.

Source: Adapted from GHARAI and VENUGOPAL, (2015).

GHARAI and VENUGOPAL (2015), explain that phenomenological models are series of equations that focus on the conservation of mass, momentum, and energy, with the knowledge of physical and chemical sub-processes that represent key conditions for the realization of the selective floatability of minerals of interest in diverse operational conditions. These models are usually a multivariate predictive control of high-quality control and highly applicable in many scenarios. For those reasons the phenomenological models are divided into three (3) groups classified as population balance (PBM), probabilistic and kinetic models.

The PBM is usually associated with three-phase-models depending on the mineral species, particle size and class, depending on the DOL.

$$DOL (\%) = \frac{\sum l_j}{\sum l_j + \sum m_j} \times 100 \quad (4)$$

Where:

- **DOL (%)** – degree of liberation in percentage.
- l_j – liberated particles of mineral species j .
- m_j – mixed particles of mineral species j .

Depending on the adapted scale, the mixed particles can be composed by 5 to 95% of two-species-particles or 0 and 100% freed particles with only mineral interest or gangue particles, showed in Figure 4-50.

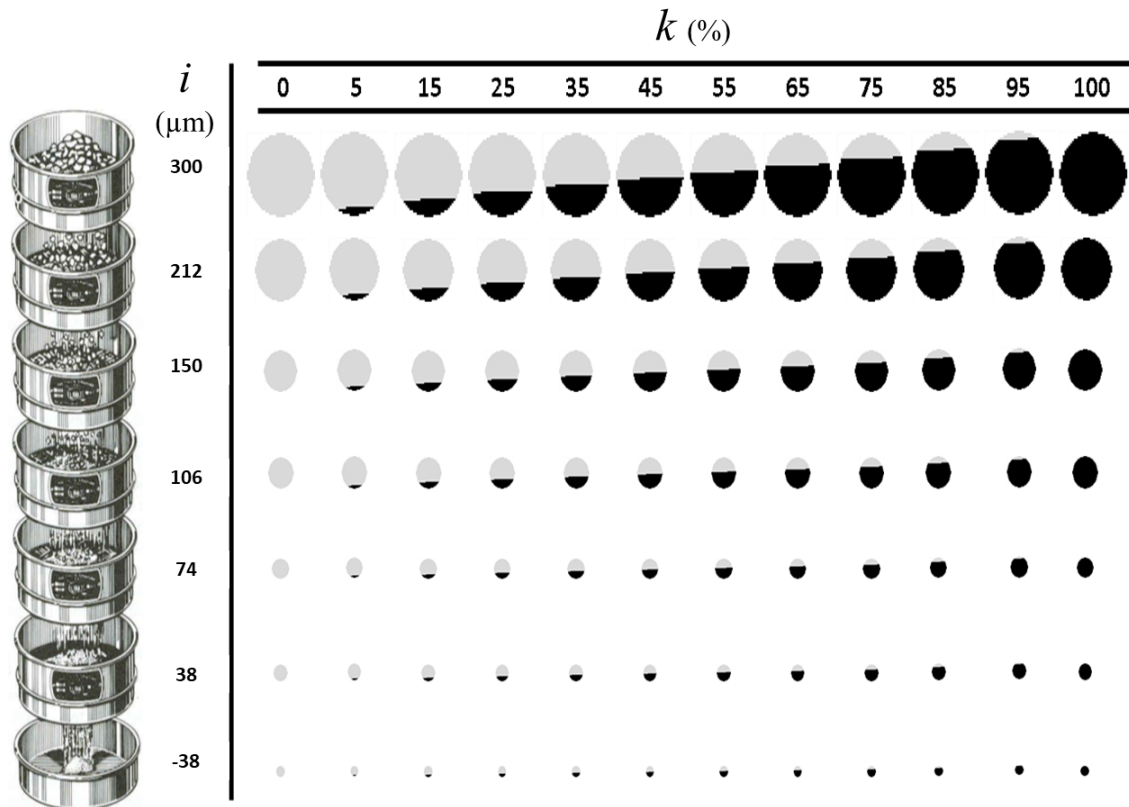


Figure 4-50: Representations of liberated and mixed particles classification species of a bi-species mineral composition.

Source: Adapted from class notes from MONTENEGRO, (2023).

The complexity of modelling flotation process is because of many physical-chemical processes happening and some key elements needed to be considered. Some of these criteria were presented by GHARAI and VENUGOPAL (2015) are three (3) main separating process after reagent hydrophobicity incidence:

1. **Aeration** – injection of air bubbles to the flotation system.
2. **Mixing** – interaction between particles and air bubbles and.
3. **Separation** – selective separation of gangue minerals, air bubbles and aggregated bubble-particle systems are directed to the top of the flotation equipment.

However, some other important criteria must be considered, namely:

4. **Degree of Liberation (DOL).**
5. **Reagent selective adsorption.**
6. **Particle and bubble size.**
7. **Bubble carrying capacity.**

8. **Water and suspended particles outlet rate.**
9. **Degree of Entrainment (ENT_c).**

When applying a feed material to an operational unit, such as a concentration operation, it is expected separation of the into two different products (P_1 and P_2), namely concentrate and reject, one with a concentration of the interest minerals and less gangue minerals and another with lower interest minerals and high gangue minerals, respectively. To guarantee that the separations is well distributed there is a need to do a mass balancing of all the product materials with the feeding materials.

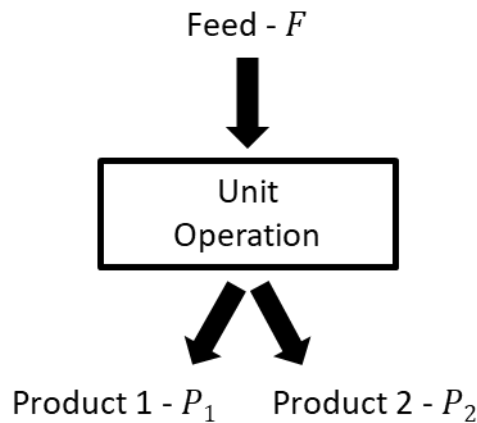


Figure 4-51: Mass distribution after single unitary operation.
Source: Adapted from class notes from MONTENEGRO, (2023)

To balance these equations, the recovery or probability must be used taking in consideration the equilibrium of all 5 levels (see Figure 4-51). To guarantee that the equilibrium system is well balanced the basic equations of transportation or transformation must be accepted:

$$F = C + T \quad (5)$$

$$F - C - T = 0 \quad (6)$$

$$\frac{F}{F} - \frac{C}{F} - \frac{T}{F} = 0 \quad (7)$$

$$1 - R_{Conc} - R_{Tail} = 0 \quad (8)$$

Equations $F = C + T$

$$(5 \text{ to } 1 - R_{Conc} - R_{Tail} = 0$$

(8 represent the mass balancing equations needed to guarantee a well-done mass

balancing of ore and water. However, there is still the need to enclose the metal grade and this can be executed using the following equations:

$$Ff_j = Cc_j + Tt_j \quad (9)$$

$$Ff_j - Cc_j - Tt_j = 0 \quad (10)$$

$$\frac{Ff_j}{Ff_j} - \frac{Cc_j}{Ff_j} - \frac{Tt_j}{Ff_j} = 0 \quad (11)$$

$$1 - R_{Conc_j} - R_{Tail_j} = 0 \quad (12)$$

Where j can be used as a mineral species or mineral grade.

The operation unit will therefore express a mass transfer of j -th component to the concentrate as by the need to a recovery of component j that can be expressed by:

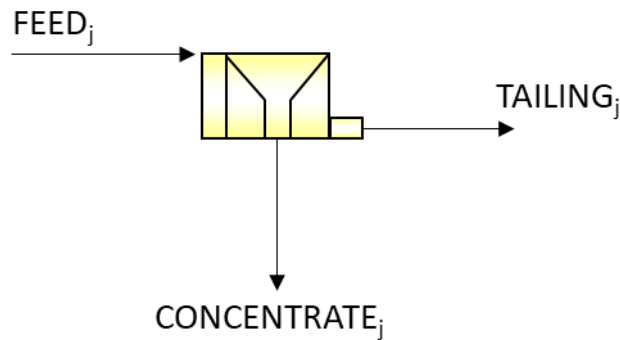


Figure 4-52: Mass conservation of j component feed to concentrate and trailing of flotation as an unit operation.
Source: Adapted from RADMEHR et al., (2018).

$$Cc_j = R_{Conc_j} \times Ff_j \quad (13)$$

$$Tt_j = (1 - R_{Conc_j}) \times Ff_j \quad (14)$$

$$Tt_j = R_{Tail_j} \times Ff_j \quad (15)$$

1.4.2 Flotation Probability using factorial design

The probability of an efficient flotation recovery can be related to a series of probabilistic events, such as collision and adhesion of particles and air bubbles, transport from the pulp to the foam zone and probability of collection (SILVA, 2015; GHARAI and VENUGOPAL, 2015). With that note, the probability of recovery of a particle (P_i) is given by:

$$P_i = P_c \times P_a \times F \times V \quad (16)$$

$$F = P_e \times P_f \quad (17)$$

$$P_a = \sin^2 \left(\frac{\phi_\tau}{\phi_c} \right) \quad (18)$$

Where,

- P_i – Probability of recovery of the particle i ;
- P_c – Probability of particle-bubble collision.
- P_a – Probability of particle-bubble adhesion.
- F – Froth stability factor and.
- V – Cell volume, m^3 .
- P_e – Probability of levitation to the base of the froth column without disengagement of particle and bubble.
- P_f – Probability of drainage from the froth.

SOUZA (2020) details that there are many kinetic models, and many can be used to apply mathematical methods to predict the scale-up to industrial plant in terms of concentrate grade and recovery, from laboratory results. SILVA (2015) complements when explaining that the kinetic-probabilistic are used as a substitute for the probabilistic models. These models correlate the flotation rate as a parameter characteristic of the flotation cell. The basic model consists of is (SOUZA, 2020):

$$\frac{dC}{dt} = -kC^n \quad (19)$$

Where,

- C – Concentration of particles.
- k – Kinetic constant.
- n – Reaction order.

The order can correlate to the first-order kinetic ($n = 1$), second-order kinetic ($n = 2$) or nonintegral-order kinetics, and are presented as:

$$\frac{dC}{dt} = -K_1 C \quad (20)$$

$$R = R_{\infty}(1 - e^{-K_1 t}) \quad (21)$$

$$R = 1 - e^{-Kt} \quad (22)$$

As explained by SILVA (2015), in the case of perfect mixtures the material recovered in the cross-section presents residence time (τ) and independently of the point in the cross-section equipment the particle concentration is the same, given that the mixture coefficient is infinity. In this case, the mineral recovery can be represented as:

$$R = \frac{K\tau}{K\tau + 1} \quad (23)$$

Where,

- R – Mass recovery.
- K – Kinetic constant.
- τ – Residence medium time (min).

GHARAI and VENUGOPAL, (2015), denote that first-order rate equation or with a few alterations can be used for batch, semi batch and continuous flotation tests. Conducting these tests can be considerable for ideal mixing, with the focus of comparing industrial cell results with different flotation equipment's and parameters. Industrially, the best approach of recovery is given by equation 24 proposed by FINCH and DOBBY (1990), where there is an intercorrelation between recoveries in the collection (R_c) and froth (R_f) zones, and these are considered independent from one another:

$$R = \frac{R_c R_f}{1 - R_c(1 - R_f)} \quad (24)$$

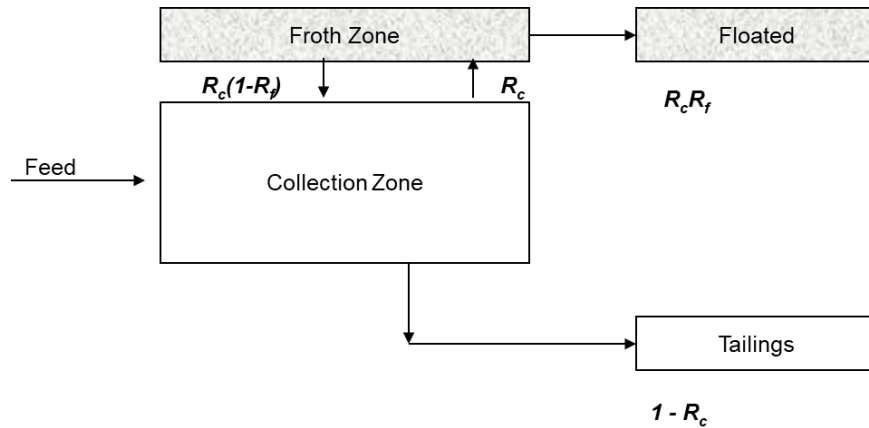


Figure 4-53: Schematics of collection and froth zone in column flotation.

Source: Adapted from FONSECA, (2022).

The use of response surface models (RSM) in the floatability of spodumene ores have been widely used as part of the Central Composite Design (CCD) method fitting for a second-order polynomial model response (KAWENSKI COOK; AGHAMIRIAN; GIBSON, 2023; CAO et al., 2021).

The CCD can be used to determine the RSM for grade and recovery of lithium ores, however, some key figures must be considered such as number of factors (k) number of blocks, number of replicas for corner points and number of centre points per block, and number of generators (p), where the factorial design can be calculated using 2^{k-p} and can the number of runs can vary depending on the number of factors such as:

		Number of Factors													
		2	3	4	5	6	7	8	9	10	11	12	13	14	15
Number of Runs	4	2^2	2^{3-1}												
	8		2^3	2^{4-1}	2^{5-2}	2^{6-3}	2^{7-4}								
	16			2^4	2^{5-1}	2^{6-2}	2^{7-3}	2^{8-4}	2^{9-5}	2^{10-6}	2^{11-7}	2^{12-8}	2^{13-9}	2^{14-10}	2^{15-11}
	32				2^5	2^{6-1}	2^{7-2}	2^{8-3}	2^{9-4}	2^{10-5}	2^{11-6}	2^{12-7}	2^{13-8}	2^{14-9}	2^{15-10}
	64					2^6	2^{7-1}	2^{8-2}	2^{9-3}	2^{10-4}	2^{11-5}	2^{12-6}	2^{13-7}	2^{14-8}	2^{15-9}
128							2^7	2^{8-1}	2^{9-2}	2^{10-3}	2^{11-4}	2^{12-5}	2^{13-6}	2^{14-7}	2^{15-8}

 Full Factorial Design	 Resolution IV Design
 Resolution V (or Higher) Design	 Resolution III Design

Figure 4-54: 2^k level factorial design.

Source: https://help.reliasoft.com/weibull20/two_level_factorial_designs.htm

The response will depend on the predictive model response (Y) and can be depicted following the second-order polynomial function below:

$$Y(\%) = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_1 \beta_2 x_4 + \beta_1 \beta_3 x_5 + \beta_2 \beta_3 x_6 + \beta_1 \beta_2 \beta_3 x_7 + \varepsilon \quad (25)$$

Where, β_0 is the constant coefficient, β_1 , β_2 and β_3 are the parameters of variation, and x_1 , x_2 , ..., x_7 are the variables and ε is the residual.

5. METHODOLOGY

The methodology of this dissertation consists of five steps: mineralogical preparation and characterization, granulometric analysis, bench-scale test, pilot-scale test, calibration, and process optimization. The tests were carried out at the Department of Mining Engineering at the School of Engineering in the Federal University of Minas Gerais (DEMIN – UFMG) laboratories listed below and external laboratories:

- **LTM** – Laboratory of Mineral Treatment.
- **LFI** – Laboratory of Interfaces Phenomena.
- **LCMM** – Laboratory of Mineral and Materials Characterization.
- Laboratory of Geometallurgy and Process Simulation.

Over 90 kg of spodumene ore samples used over this work was provided by a mining company. From which, 50 kg was from the flotation feed, 20 kg of the concentrated product and 20 kg from the tailing product. The samples were previously fragmented (crushed and milled), classified and deslimed. The flotation feed sample is a blend of 50 % of tailings dam 1 & 2, and other 50 % of tantalum tailings plants (TaP 1 & 2), shown Figure 4-28.

Important to note that the chemical analysis was performed in two different methods one a semi-quantitative Wavelength Dispersive X-Ray Fluorescence (WDXRF) to quantify more heavy elements such as Si, Al, Fe, Na, K, Ca, Mg, Mn, P, Ti etc, and their respective oxides SiO_2 , Al_2O_3 , Fe_2O_3 , Na_2O , K_2O , CaO , MgO , MnO , P_2O_5 , TiO_2 , etc, respectively. On the other hand, the inductively coupled plasma – optical emission spectrometry (ICP-OES) for Li as it is one of the lightest elements (see section 1.2) and isn't detectable by XRF and the preparation of the analysis can contaminate due to the flux composition.

1.5 MINERALOGICAL PREPARATION AND CHARACTERIZATION

1.5.1 Ore sampling

The samples were carefully homogenised and divided into smaller samples of 500 g, 300 g and 10g and rest to archive.

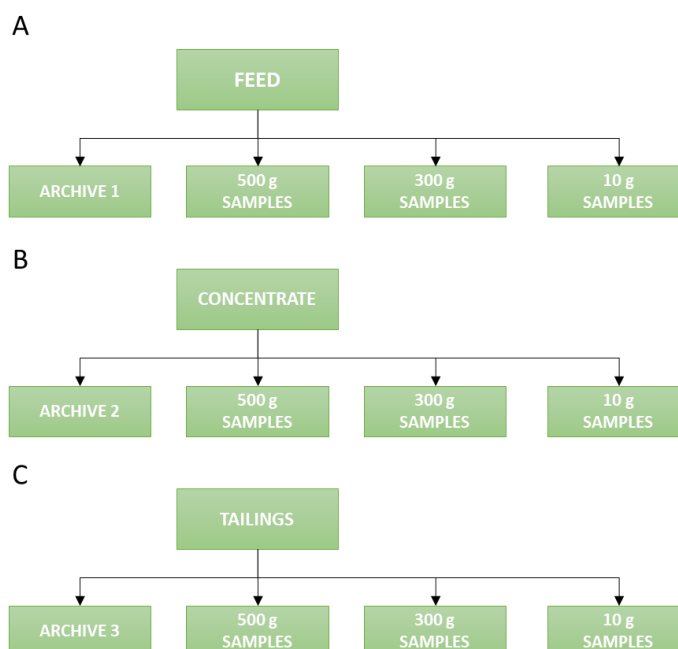


Figure 5-1: Sample preparation and separation of the flotation (A) feed, (B) concentrate and (C) tailings.

Source: Developed by the author.

1.5.2 Mineralogical Analysis by XRD

The mineralogical phase identification consisted of the use of 10 g sample of the sample previously pulverised ($-38\ \mu\text{m}$) in the LTM. A fraction of the sample was introduced to the X-Ray Diffractometry by method of mass spectrometry, model PW 3710 from PHILIPS-PANalytical (Figure 5-2) in the LCM, copper (Cu) X-ray lamp with $\lambda\alpha=1.5406\ \text{\AA}$ wavelength. The XRD settings configuration are presented in Table 5-1.

Table 5-1: XRD parameters for mineralogical analysis.

PARAMETER	VALUE	UNIT
Voltage	50.0	kV
Current	35.0	mA
Angle range	3.00 – 90.00	°
Scan speed	0.06	°/s
Incidence angle	20	°

Source: Developed by the author.



Figure 5-2: X-Ray Diffractometry, Model PW 3710 Philips-PANalytical from Malvern Panalytical.

The processing of the resulting data was done using the HighScore Plus software. And mineralogical phase semi-quantitative results were determined by the Rietveld method.

1.5.3 Chemical Analysis by WDXRF

For the chemical analysis a 10 g sample previously pulverised ($\sim 38 \mu\text{m}$) in the LDTM. A fraction of mass was used to produce a molten tablet with a flux from OregonTM P0441E of 1/10 (sample/flux), composed of 66.17% of lithium tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$), 33.33% of lithium metaborate (LiBO_2) and 0.50% lithium iodate it was also added 1g of lithium nitrate (LiNO_3) as oxidising agent in the LCM. The fusion was carried out by an electrical fusion machine model C1 from NiekaTM, with fusion settings configurations presented in Table 5-2.

Table 5-2: Fusion machine program for molten tablet preparation.

	Steps							
	0	1	2	3	4	5	6	7
Time (min)	00:15	03:10	03:00	03:00	00:45	01:00	02:00	02:05
Temperature (°C)	700	750	1250	1250	900	0	0	0
Stirring (%)	0	0	30	90:30	0	0	0	0
Cooling (%)	0	0	0	0	0	0	50	70

Source: Developed by the author.



Figure 5-3: Electrical fusion machine C1 - Nieka™.



Figure 5-4: ARLTM PERFORM'X model GEN-X 4200W semi-quantitative WDXRF analyser from Thermo Scientific™.

After the molten tablet cooling the analysis was carried out using the Wavelength Dispersive X-Ray Fluorescence (WDXRF) with the ARL™ PERFORM'X, model GEN-X 4200W from Thermo Scientific™, using a rhodian tube (5GNf Rh 50 u) with X-Y automatic manipulator. The processing of the results was done by OXSAS and UniQuant software. The loss on ignition (LOI) was done using the calcination of the sample.

1.5.4 Chemical Analysis by ICP-OES

Preparation of lithium chemical analysis consisted of using a fraction of the 10 g sample previously pulverised ($-38\ \mu\text{m}$) in the LTM and leached in different acids. A sample is digested by four (4) acids namely, concentrated nitric acid solution (HNO_3 , 65% purity), concentrated hydrochloric acid solution (HCl , 20%), perchloric acid solution (HClO_4 , 70%) and hydrofluoric acid (HF) before analysis of the Li element by the ICP-OES Optical Emission Spectrometer 8300 PerkinElmer (Figure 5-5).



Figure 5-5: Inductively Coupled Plasma - Optical Emission Spectroscopy Model Optima Series 8300 by Perkin Elmer.

All preparation and analysis were carried out by external laboratories. The ICP-OES equipment settings for the analysis were as followed in the

Table 5-3.

Table 5-3: ICP-OES parameters for Li chemical element analysis, for Perkin Elmer – Optima Series 8300.

PARAMETER	VALUE	UNIT
Power	1.5	kW
Plasma flow	15.0	L/min
Nebuliser pressure	0.7	L/min
Visualization height	10	mm
Replicate reading time	5	s
Stabilisation time	15	s
Interval between samples	30	s
Pump flow rate	15	rpm
Inlet time	10	s
Replicas	3	-

Source: Adapted by the author, developed by external laboratories.

1.6 PARTICLE SIZE DISTRIBUTION (PSD)

The granulometric analysis was done using 150g samples and done in duplicate. The screens used followed the Tyler series of 600, 425, 300, 150, 106, 75, 53 and 38 μm screens in this specific order, using the suspended vibrating screens (Figure 5-8), in the LTM. Screening was carried out for about 30 minutes with a water flow of 1.0 L/min. Afterwards the retained was dried and weighted.



Figure 5-6: Variety of different screens diameters.



Figure 5-7: Example of functionality of the granulometric screen procedure.



Figure 5-8: Suspended vibrating laboratory-scale screen.

The vibration was carried out for 30 min, afterwards, each retained mass was carefully weighted to minimize the loss. The results were added to MS Excel Spreadsheet for analysis, interpretation, and graph design.

1.7 FLOTATION

1.7.1 Bench-Scale Test

The flotation bench-scale tests were carried out using a 500 g feed samples, using the mechanical cell from Denver, model D12, in the LFI.

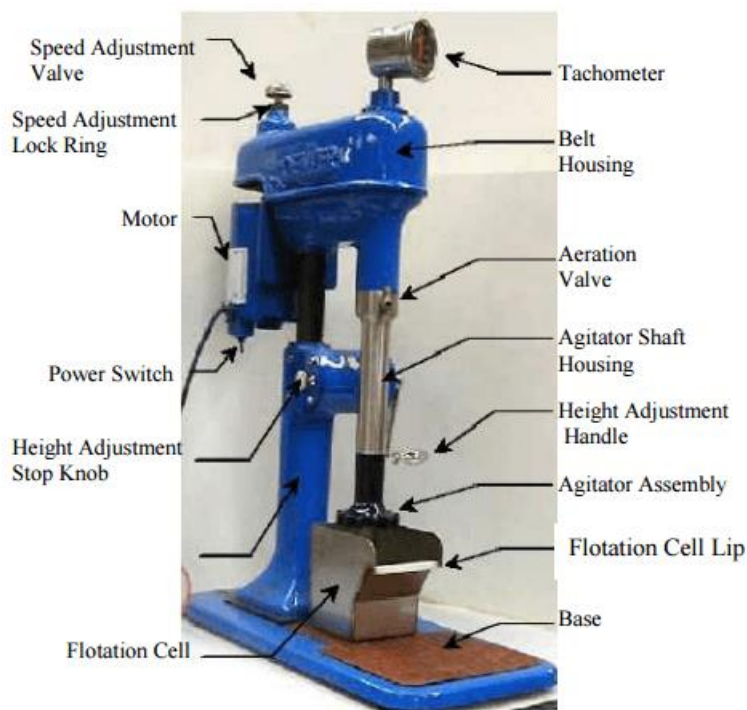


Figure 5-9: Schematics of the D12 flotation cell from Denver.
Source: MICHAUD, (2015).

Some operational and variable setting configuration were preestablished following the literature reviews and reagent supplier recommendation, presented in Table 5-4. The collector used was Clariant's FLOTINOR 17695 anionic collector of fatty acid composition, the pH regulators use was HCl and NaOH with concentration (v/v) of 1% and 10%. The tests were designed following the design of experiment presented in Table 5-5. The concentrate of the rougher flotation will be the feed of the cleaner flotation to optimize the grade and recovery of spodumene for market specifications.

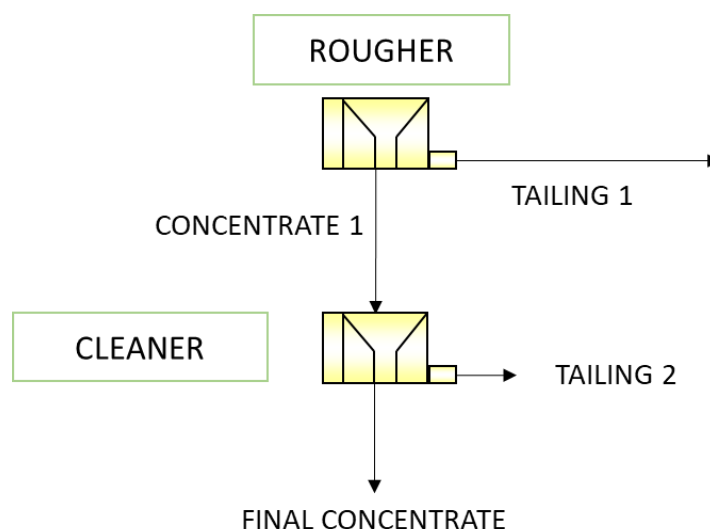


Figure 5-10: Flotation sequence and products.

Source: Developed by the author.

Table 5-4: Operational conditions and configurations for bench tests.

PARAMETER	VALUE	UNIT
Airflow	1,000	L/min
Cube volume	1.5 (1,500)	L (cm ³)
% Solid Conditioning	50	%
% Solid Rougher Flotation	30	%
Conditioning time	120 (2)	s (min)
Flotation time	180 (3)	s (min)

Source: Developed by the author.

The results were added to MS Excel Spreadsheet and Minitab 17 for analysis, interpretation, and graph design.

Based on the first batch of trials carried out there was a need for a second batch of flotation tests in a cleaner stage, to achieve objective grade and metallurgical recovery, the conditions used are described in Table 6-6.

1.7.2 2^k Factorial Design

To minimize the extend of testing needed and maximize the results obtained, since in the first rougher testing three (3) parameter were checked, namely, the collector dosage (CD), the pH solution and the rotor rotation (RR). Minitab 17 Statistical Software was used to create a Factorial Design using the default generators, where 3 continuous (*k*) factors were established with 2 replicates per corner points and 3 centre points per block for 1 block, resulting in the following equation to determine the number of $2 \times 2^k + 3$. The result came out with 19 runs and are presented below:

Table 5-5: Factorial design for rougher flotation tests.

Factor	Lower level (-1)	Centre point (0)	Higher level (+1)
pH	7	9	11
CD	600	800	1,000
RR	800	1,000	1,200
Test ID	pH	CD	RR
AML-01	0	0	0
AML-02	-1	1	-1
AML-03	1	-1	1
AML-04	-1	-1	-1
AML-05	-1	-1	-1
AML-06	1	1	1
AML-07	-1	1	1
AML-08	-1	1	1
AML-09	-1	-1	1
AML-10	1	-1	1
AML-11	1	1	-1
AML-12	1	-1	-1
AML-13	-1	-1	1
AML-14	1	1	1
AML-15	1	-1	-1
AML-16	1	1	-1
AML-17	-1	1	-1
AML-18	0	0	0
AML-19	0	0	0

Source: Developed by the author.

6. RESULTS & DISCUSSION

1.8 MINERALOGICAL COMPOSITION

In this section the results of mineralogical composition are presented for the industrial flotation feed, concentrate and tailing samples.

Figure 6-1 shows the mineralogical composition of the flotation step for the SP plant, where it is composed of quartz (SiO_2), spodumene ($\text{LiAl}(\text{Si}_2\text{O}_6)$), albite ($\text{Na}(\text{AlSi}_3\text{O}_8)\text{Ab}_{90}\text{An}_{10}$), muscovite ($\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_8$) and microcline ($\text{K}(\text{AlSi}_3\text{O}_8)$).

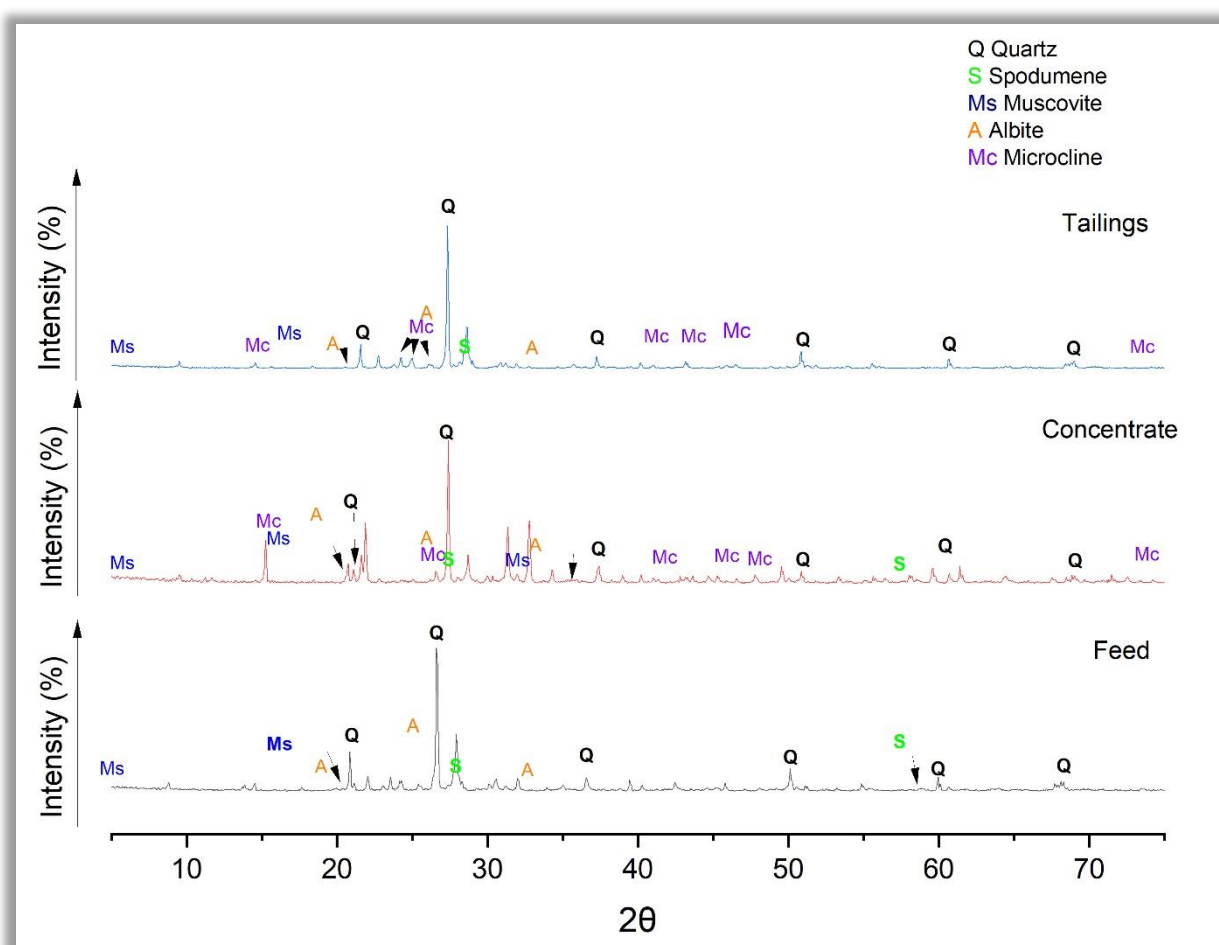


Figure 6-1: XRD spectrum for spodumene flotation feed, concentrate and tailings.

Source: Developed by the author.

The feed was majorly composed of albite (41.8%) and quartz (37.2%) making for 79% of the sample followed by minor minerals such as spodumene (11.4%), muscovite (9.6%) and traces of microcline (0.1%). Concentrate samples are composed of majority of spodumene (59.6%) and quartz (24.1%) followed by traces of albite (7.7%), muscovite (6.5%) and microcline (2.1%). The tailings were composed in its majority by albite (45.9%) and quartz (38.0%) and muscovite (8.6%), microcline (7.3%) and spodumene (0.3%). ASSUMPÇÃO (2015) describe these minerals as the basic composition of pegmatite bodies, other minerals such as zinnwaldite,

plagioclase ($\text{Ab}_{100}\text{An}_0$) and as well as cassiterite (SnO_2) and columbite-tantalite ($(\text{Fe,Mn})\text{Nb}_2\text{O}_5$ - $(\text{Fe,Mn})\text{Ta}_2\text{O}_5$) as members of the microlite group. Still ASSUMPÇÃO (2015) explains as the most abundant mineral as quartz (31%), followed by spodumene (28%), albite (16%) and microcline (13%), traces of lepidolite ($\text{K}_2\text{Li}_3\text{Al}_3(\text{AlSi}_3\text{O}_{10})_2(\text{OH,F})_4$) (11%) were also found.

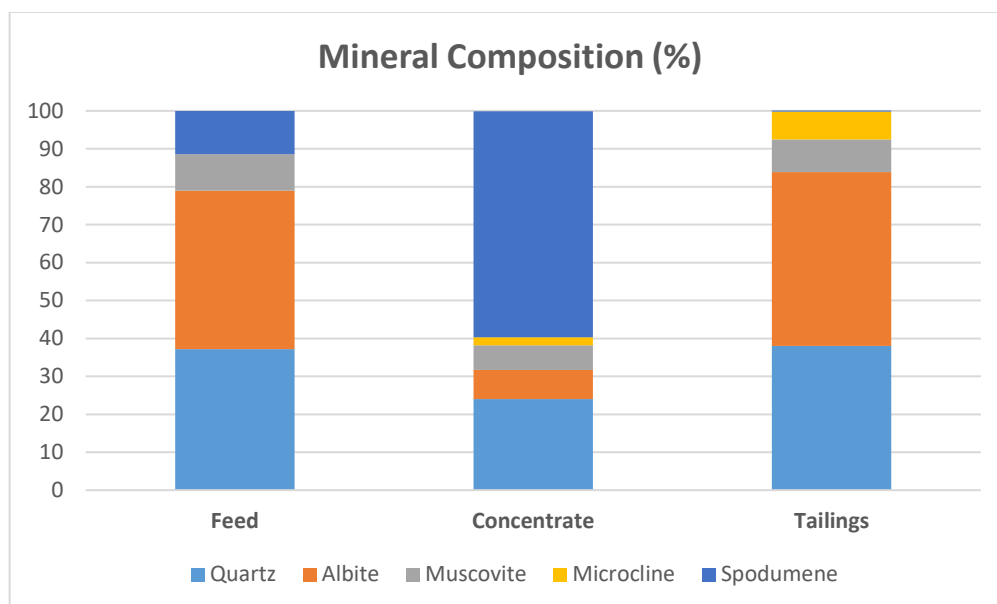


Figure 6-2: Mineralogical composition of flotation feed, concentrate and tailings of SP Plant.
Source: Developed by the author.

1.9 PSD AND CHEMICAL ANALYSIS

Chemical analysis results of these the products carried out in combined XRF and ICP technics are shown in the figures below, comparison with XRD results is evident depicting that all technics are coherent with each other.

Table 6-1: Grade distribution of feed, concentrate and tailings from flotation SP Plant.

OXIDE (%)	Li_2O	SiO_2	Al_2O_3	Na_2O	MgO	Fe_2O_3	MnO	CaO	K_2O	F	P_2O_5	Rb ₂ O (ppm)
Feed	1.01	75.27	14.80	4.75	0.09	0.37	0.00	0.45	1.89	0.00	0.09	0.48
Concentrate	4.72	68.44	24.56	0.88	0.59	1.05	0.00	2.18	0.73	0.00	0.44	0.20
Tailings	0.35	75.70	13.63	5.58	0.05	0.21	0.10	0.17	2.15	0.00	0.05	0.70

Source: Developed by the author.

Note that about Li_2O in feed material is about 1.01% with Si_2O of 75.27, Al_2O_3 of 14.80% and Fe_2O_3 of 0.37%, this represents a lower lithium oxide grade presented by SOARES (2021) however with similar amount of Fe_2O_3 (0.3%) in the feed samples. These grades are higher than those found by ASSUMPÇÃO (2015), 0.7%, and low than those found by SOARES (2021), 1.3%, however given that the feed material is a combination of the Ta Plant and tailing dams 2

and 3, it shows that it is in accordance with source materials. COOK and GIBSON (2023) when presenting several average lithium head grades around the world we see grades as low as 0.91%, in development in Canada, and high as 2.80%, in operation in Australia.

Side-by-side comparison of the XRD spectral data with the chemical analysis illustrates a very similar behaviour with a minimum deviation. For the feed comparison (Figure 6-3) less than 0.1% deviation can be seen between the Li_2O analysis, the highest difference can be seen for the SiO_2 of greater than 2% and the XRD did not find any iron-bearing mineral.

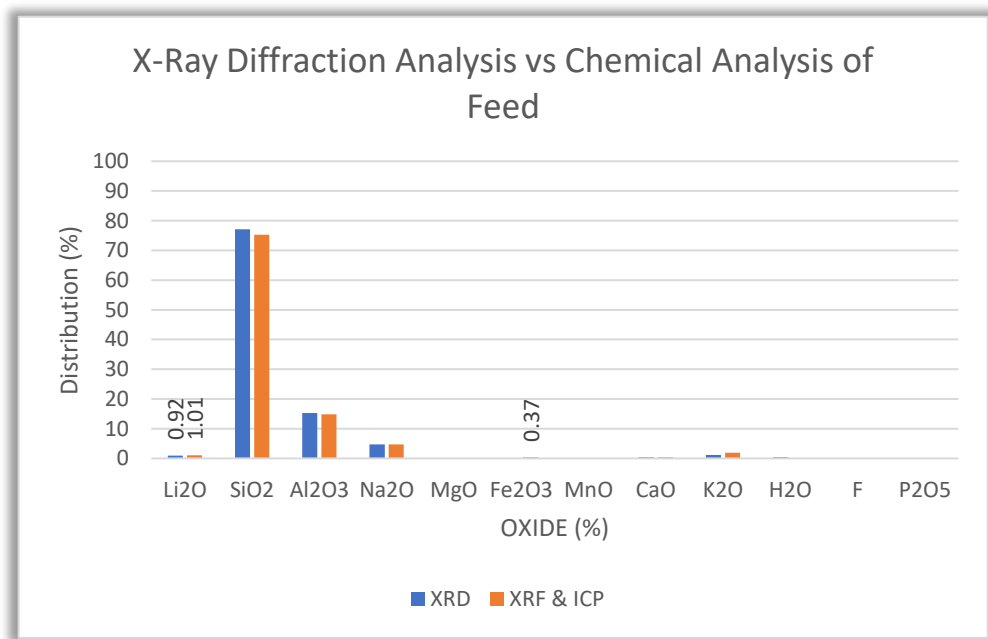


Figure 6-3: Spectral analysis (XRD) vs chemical analysis (ICP & XRF) of feed.

Source: Developed by the author.

For the concentrate samples there was an equivalent grade of Li_2O , the silica difference was just above 4% and lesser for alumina, and there was an increase of Fe_2O_3 grade.

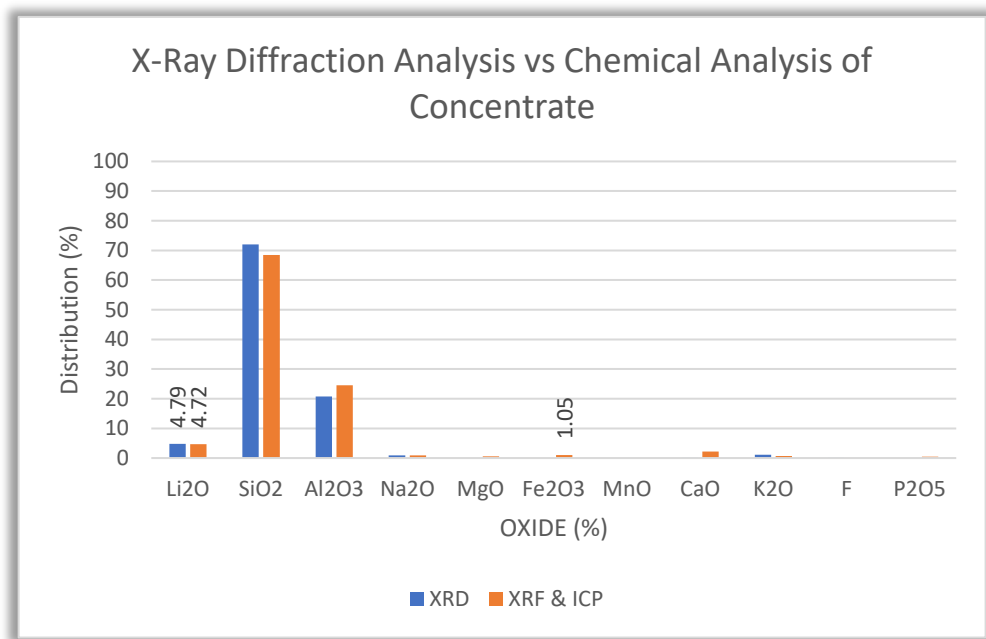


Figure 6-4: Spectral analysis (XRD) vs chemical analysis (ICP & XRF) of concentrate.
Source: Developed by the author.

The largest difference of lithium oxide grade can be seen in the tailings of 0.30%, this is related to the XRD limitation of identification of trace minerals. Silica had a small gap between the two technics and iron oxide in is lesser than 0.50%.

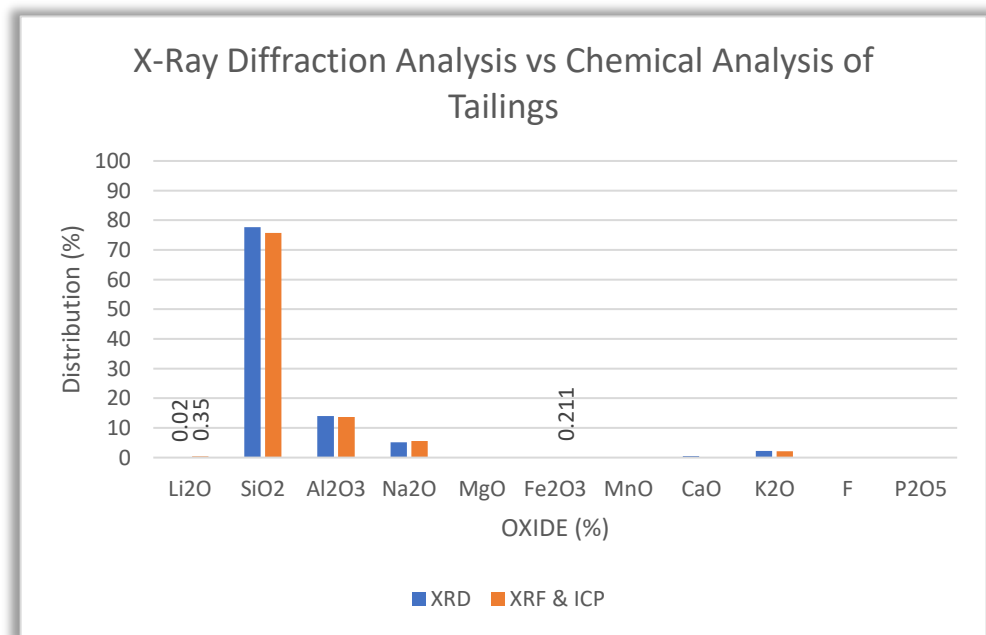


Figure 6-5: Spectral analysis (XRD) vs chemical analysis (ICP & XRF) of tailings.
Source: Developed by the author.

PSD distribution of the three samples (Figure 6-6) show that top size is about 600 μm , some traces can be found in about 400 μm . The concentrate is finer, about 90.46% is below 150 μm , when compared to the feed (70.31%) and the tailings (67.58%). Using RR distribution model, it's easy to see that the k factor or d_{50} for feed material is around 119 μm with m factor equal 2.03, while the concentrate as k and m equal to 84 μm and 2.06, respectively, in the other hand, the tailings have k and m equal to 126 μm and 2.12. Further below it is presented the relation between PSD and chemical composition.

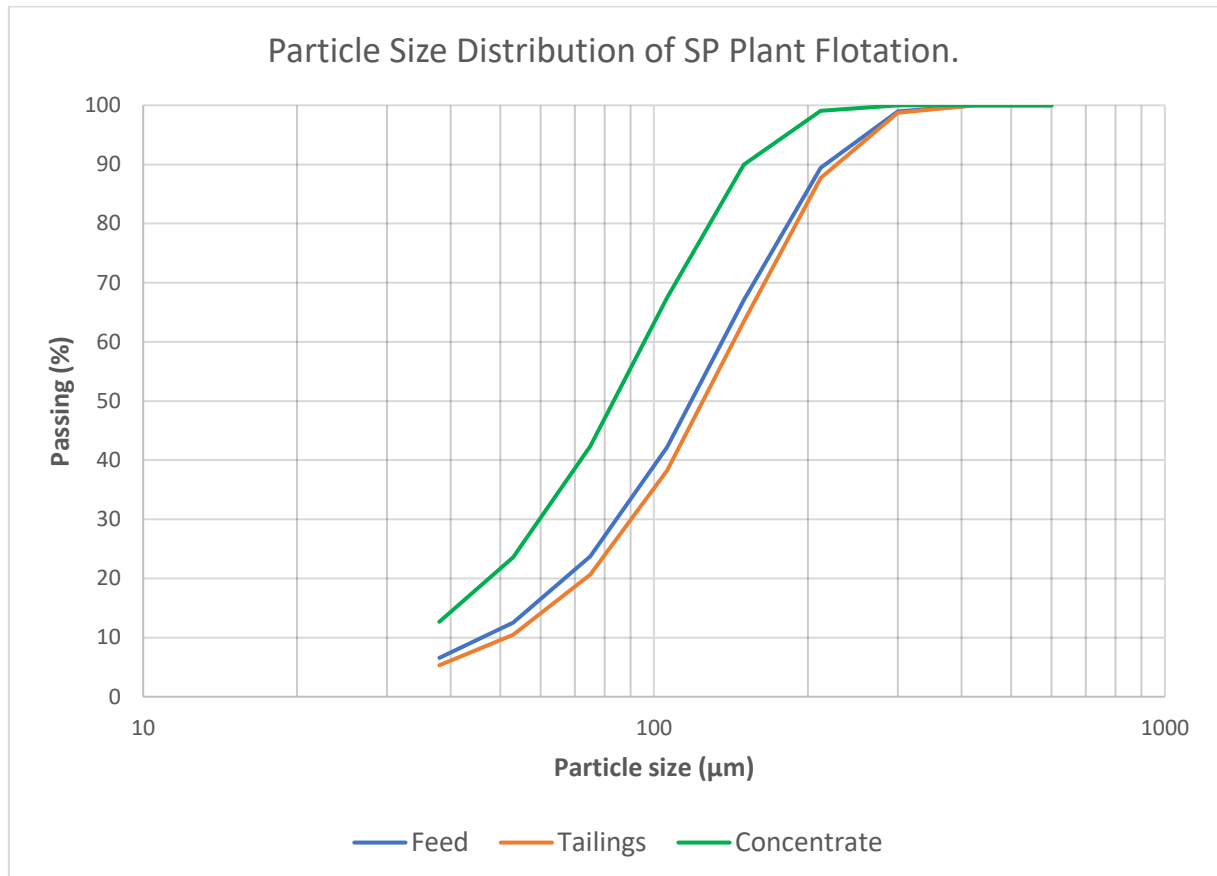


Figure 6-6: PSD of flotation samples from SP Plant.
Source: Developed by the author.

When analysis the distribution for granulometric ranges it shows that there isn't any significant variation on the Li_2O along the various ranges for the feed material, and as expected the more fineness material as the highest grade (1.18%), Fe_2O_3 (0.64%) behaves accordingly with de lithium oxide, as the lithium oxide increases with fineness so those the iron oxide. Naturally, as the lithium grade increases the silica oxide and alumina decreases.

Note that despite spodumene having a coarse DOL (about 250 μm , see section 1.2.4.2), flotation mainly occurs in finer particles, $90.0\% < 150 \mu\text{m}$, as of particles with $+150 \mu\text{m}$ have more about 1.05% Li_2O and about 0.59% Fe_2O_3 .

Table 6-2: Grade distribution by granulometric ranges for feed, concentrate and tailings from SP Plant.

SAMPLE	Li ₂ O (%)	SiO ₂ (%)	Al ₂ O ₃ (%)	Fe ₂ O ₃ (%)	Na ₂ O (%)	K ₂ O (%)	CaO (%)	MgO (%)	MnO (%)	P ₂ O ₅ (%)	TiO ₂ (%)
Feed +150µm	1.05	74.39	13.94	0.59	3.80	2.18	0.24	0.04	0.15	0.07	<0.01
Feed -150µm +38µm	1.12	75.79	13.39	0.53	4.19	1.44	0.41	0.05	0.09	0.10	0.04
Feed -38µm	1.18	70.95	14.42	1.16	3.65	1.79	1.06	0.42	0.11	0.15	0.11
FEED	1.11	74.69	13.70	0.64	4.00	1.70	0.45	0.10	0.11	0.10	0.04
Concentrate +150µm	5.76	64.68	22.32	0.99	0.77	0.47	1.39	0.21	0.17	0.52	0.07
Concentrate -150µm +38µm	4.81	67.44	18.26	1.10	0.75	0.57	1.66	0.27	0.17	0.46	0.15
Concentrate -38µm	2.96	69.64	14.52	1.79	0.94	0.90	2.19	0.32	0.14	0.30	0.22
CONCENTRATE	4.59	67.32	18.32	1.24	0.80	0.62	1.72	0.27	0.16	0.43	0.15
Tailings +150µm	0.64	75.64	13.24	0.43	4.34	1.89	0.18	0.03	0.14	0.04	0.02
Tailing -150µm +38µm	0.45	77.90	12.32	0.45	4.84	1.51	0.19	0.03	0.07	0.04	0.02
Tailing -38µm	0.46	73.71	12.66	0.64	4.69	1.76	0.43	0.25	0.07	0.06	0.04
TAILINGS	0.52	76.71	12.68	0.46	4.65	1.67	0.21	0.05	0.09	0.04	0.02

Source: Developed by the author.

A more detailed graph is presented in Figure 6-7, where is clear that the distribution of Li₂O varies by a small amount. On one hand, PSD higher than 150 µm have an average of 0.89% with a standard deviation of 0.19%, below 150 and greater than 45 µm the average is about 0.92% a standard deviation of 0.11% and below 45 µm about 0.92%. On the other hand, iron oxide as a very different approach at 595 µm is about 1.41%, between 297 and 150 µm is about 0.68% with standard deviation of 0.11% and below 150 and greater than 45 µm is 1.38% and 0.53%, respectively, and below 45 µm is about 2.47% average.

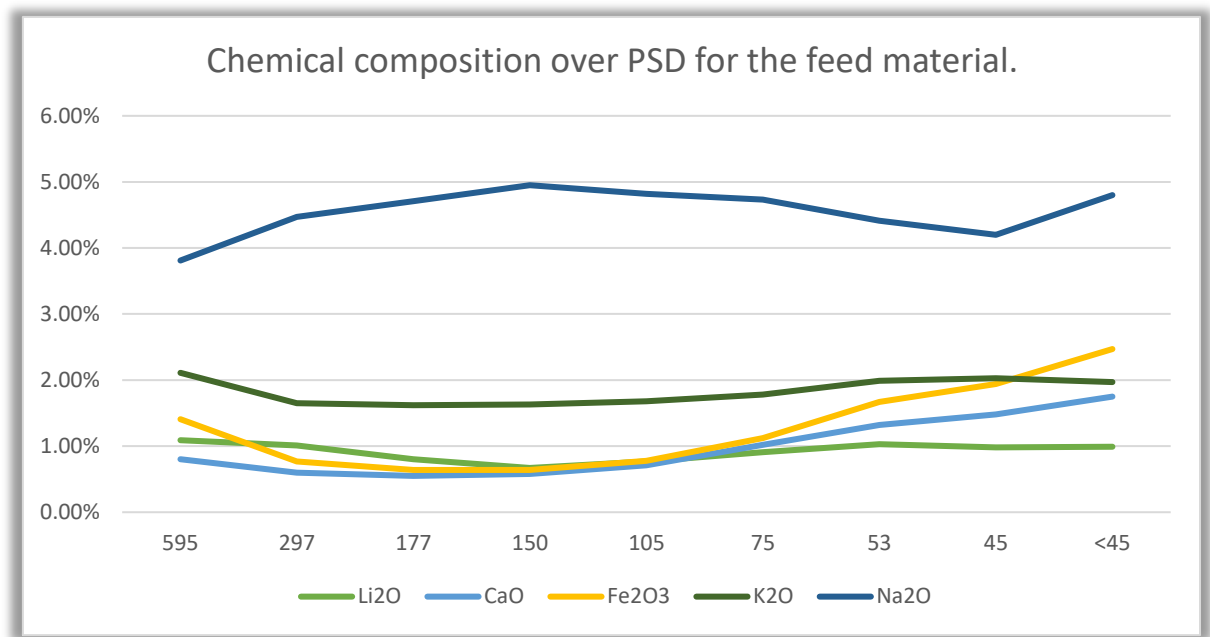


Figure 6-7: Flotation feed material PSD and chemical analysis relation.
Source: Adapted by the author.

1.10 FLOTATION TESTS

Using the DOE as a primary factor to do exploratory flotation tests, reduced the need for over usage of samples and create a more diversely spread range of tests. The results of the 2^k can be seen in Table 6-3, show the concentrate grade and recovery for each test in terms of Li_2O , SiO_2 and Fe_2O_3 . When looking at the grade of Li_2O of the concentrate tests AML-11 had the highest concentrate grade (4.66%) with just a 56% recovery, however, is had one of the lowest SiO_2 and Fe_2O_3 recoveries with 11.72% and 26.90%, for 66.96% and 0.93% metal grades, respectively. However, tests AML 09 and 13 had the highest Li_2O recovery of around %79 with ore grade varying from 1.75 and 1.92% on the downside, SiO_2 and Fe_2O_3 were the highest recovery around 40 – 48% and 68 – 71% and grades of about 74% and 0.50%, respectively.

Table 6-3: Grade and recovery results from 2^k flotation rougher test.

Test ID	Li ₂ O		SiO ₂		Fe ₂ O ₃		Mass Recovery (%)
	Grade (%)	Recovery (%)	Grade (%)	Recovery (%)	Grade (%)	Recovery (%)	
AML-01	2.93	69.00	70.28	23.65	0.84	54.24	25.05
AML-02	3.63	71.53	69.13	18.64	0.90	45.00	19.95
AML-03	4.02	28.35	64.78	6.51	1.75	19.90	7.30
AML-04	2.64	77.79	73.13	30.70	0.66	58.60	31.71
AML-05	0.54	37.26	75.57	27.68	0.97	60.83	27.79
AML-06	3.62	25.54	69.04	7.02	1.21	17.17	7.54
AML-07	1.85	77.63	74.91	43.98	0.49	64.83	44.07
AML-08	2.02	77.03	74.74	40.44	0.52	63.96	40.50
AML-09*	1.92	78.06	73.86	40.56	0.54	68.42	41.31
AML-10	3.66	33.28	67.37	8.72	1.28	22.86	9.50
AML-11	4.66	56.03	66.96	11.72	0.93	26.90	12.86
AML-12	4.37	25.44	63.58	5.18	1.53	14.74	5.88
AML-13	1.75	79.99	74.83	48.45	0.47	71.33	48.35
AML-14	3.17	22.85	67.21	6.89	1.25	17.76	7.52
AML-15	4.03	31.22	63.15	3.85	1.56	10.88	4.41
AML-16	4.23	16.01	62.41	3.48	1.40	9.43	4.02
AML-17	3.54	75.11	70.83	21.63	0.81	48.75	22.98
AML-18	2.15	72.41	74.99	36.57	0.56	57.52	36.46
AML-19	2.43	73.04	73.30	31.48	0.60	56.62	32.41

Source: Adapted by the author.

* - Excessive air inlet for a few seconds.

Using the regression model shown in equation (25) for Li₂O grade concentrate equation (26) with a R² of 81.93%.

$$\text{Li}_2\text{O} (\%) = -27.2 + 2.69 \text{ pH} + 0.0346 \text{ CD} + 0.0199 \text{ RR} - 0.00278 \text{ pH} * \text{CD} - 0.00166 \text{ pH} * \text{RR} - 0.000027 \text{ CD} * \text{RR} + 0.000002 \text{ pH} * \text{CD} * \text{RR} \quad (26)$$

When analysing most influential factor is shown that pH as the most importance of Li₂O grade variation followed by the RR afterwards the combination of CD and RR.

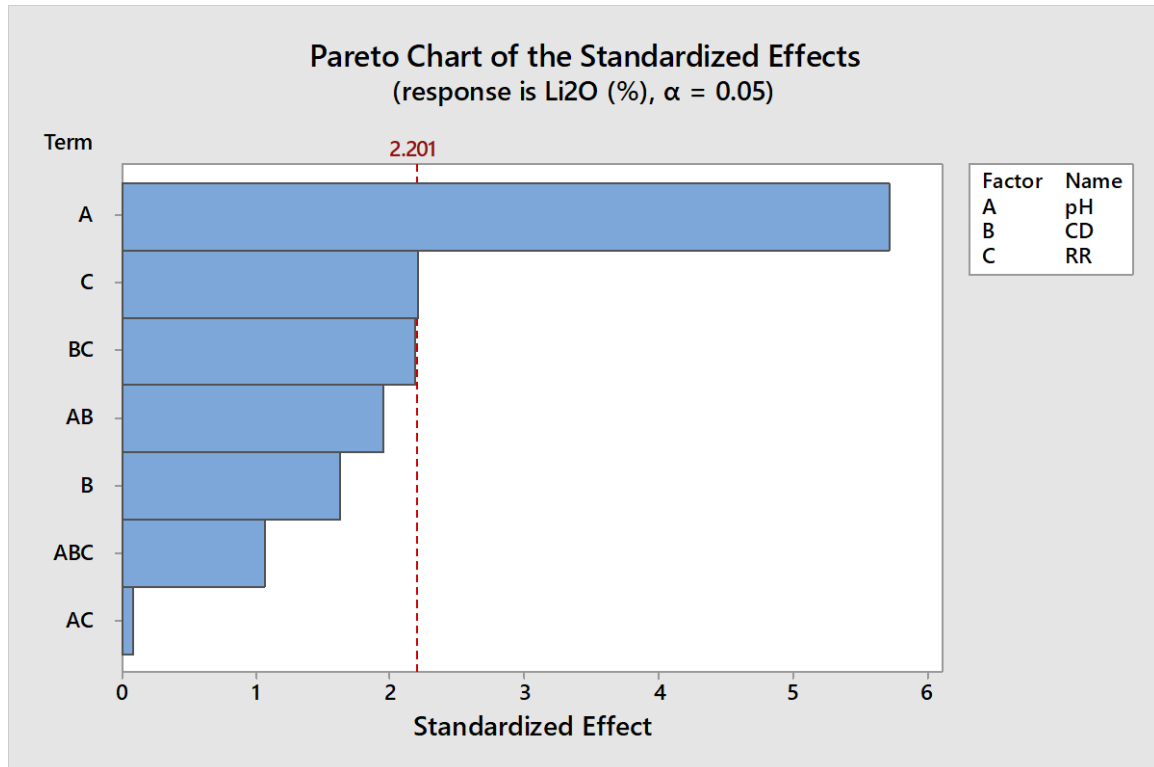


Figure 6-8: Li₂O grade influential factors in flotation.
Source: Developed by the Minitab 17.

When analysing these two factors in a surface plot and response optimizer at conditions of pH 11.0, CD 1,000 g/t and RR 800, the maximum ore recovery is about 4.35% (see Figure 6-9).

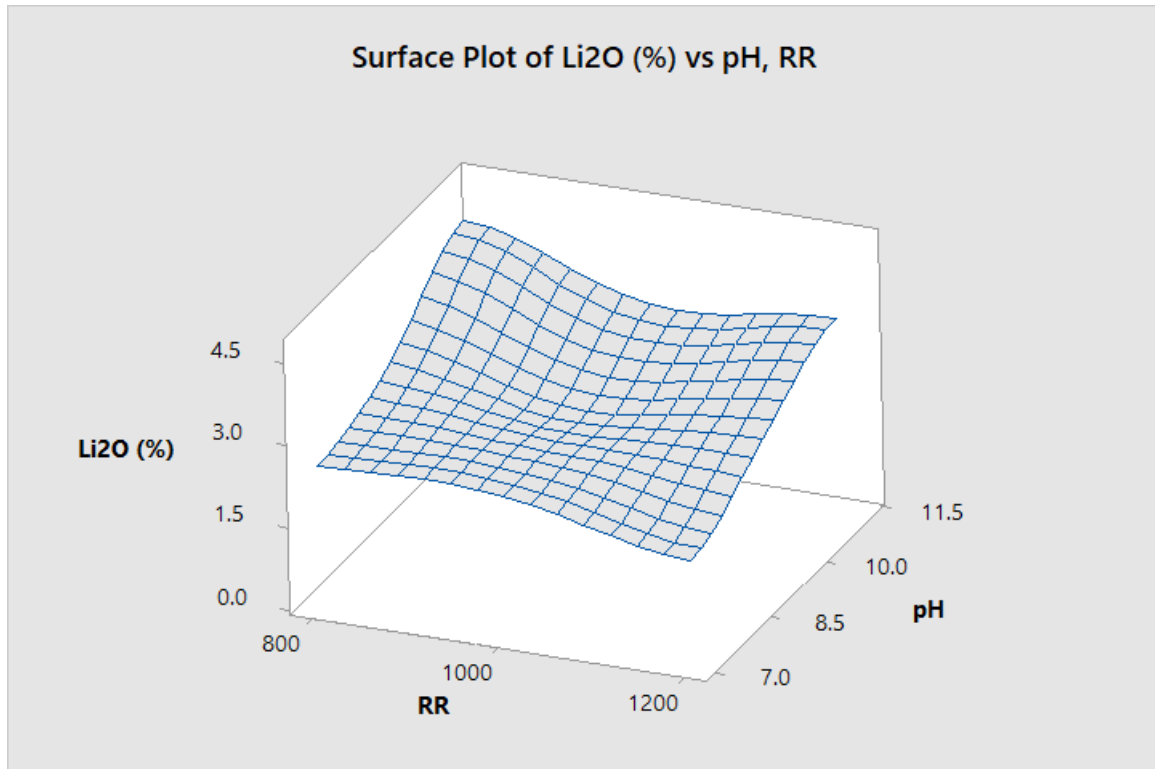


Figure 6-9: Surface plot response for Li₂O by pH vs RR.
Source: Developed by the Minitab 17.

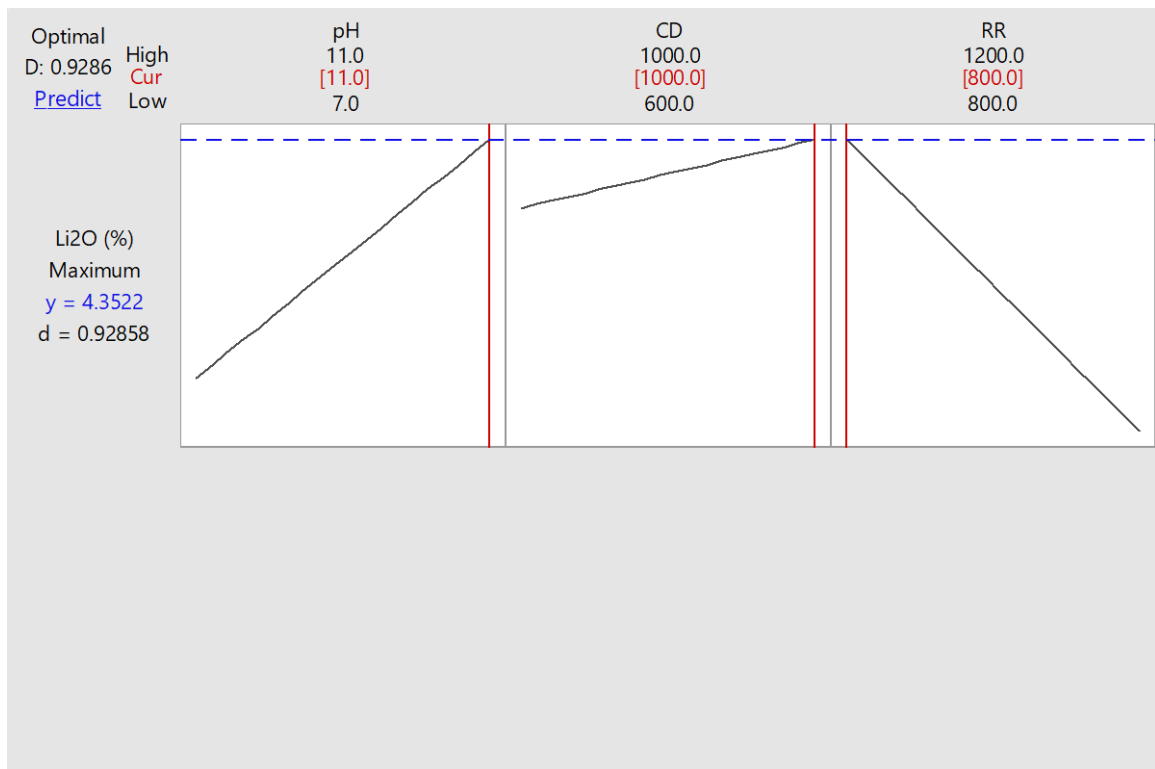


Figure 6-10: Response optimizer for Li₂O grade.
Source: Developed by the Minitab 17.

When analysing the recovery, it was shown the best recovery equation was presented in (27) with a R^2 of 73.84%.

$$\text{Li}_2\text{O rec. (\%)} = -112 + 7.6 \text{ pH} + 0.190 \text{ CD} + 0.223 \text{ RR} - 0.0090 \text{ pH} * \text{CD} - 0.0149 \text{ pH} * \text{RR} - 0.000144 \text{ CD} * \text{RR} + 0.000005 \text{ pH} * \text{CD} * \text{RR} \quad (27)$$

When analysing the factor influence for Li_2O recovery (see Figure 6-11) we can see that pH is still the most impactful factor followed by combination of pH and RR afterwards combination of CD and RR.

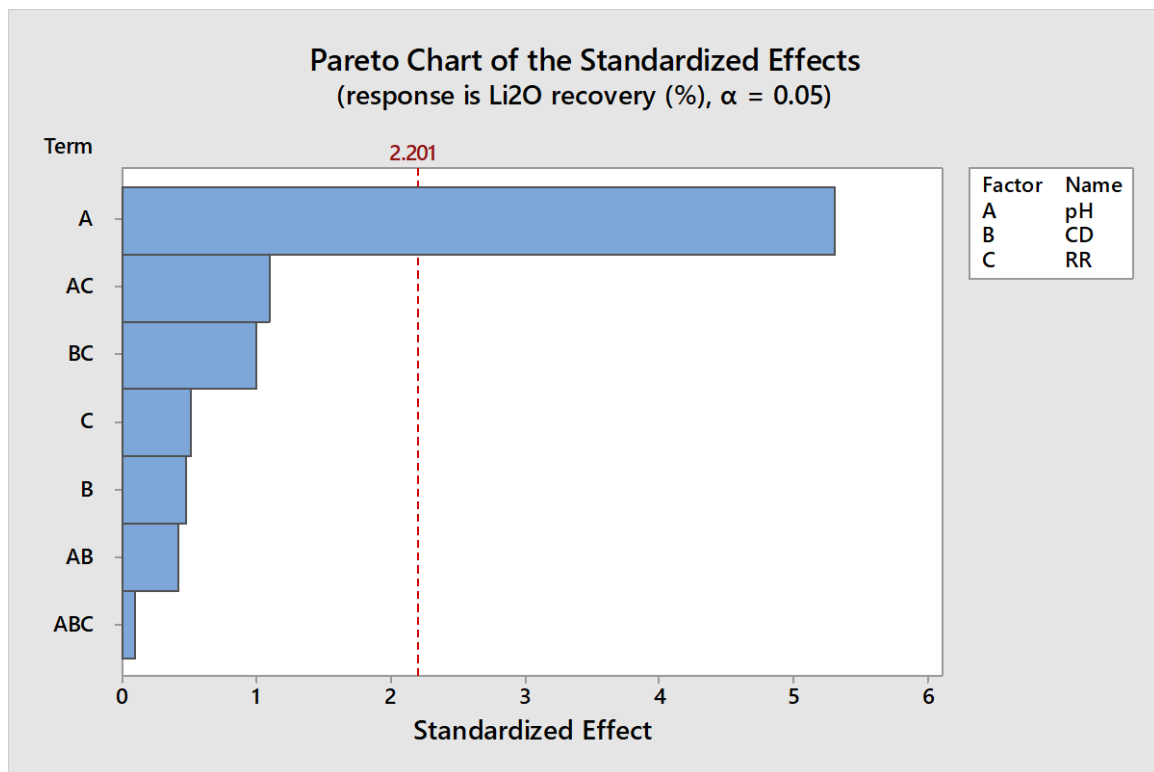


Figure 6-11: Li_2O recovery influential factor in flotation.
Source: Developed by the Minitab 17.

Comparing the reaction of Li_2O recovery for the influence of pH and RR, by surface plot and response optimizer we can see that at pH 7.0, with CD of 600 g/t and RR 1200 rpm, we can achieve about 82.28% of recovery.

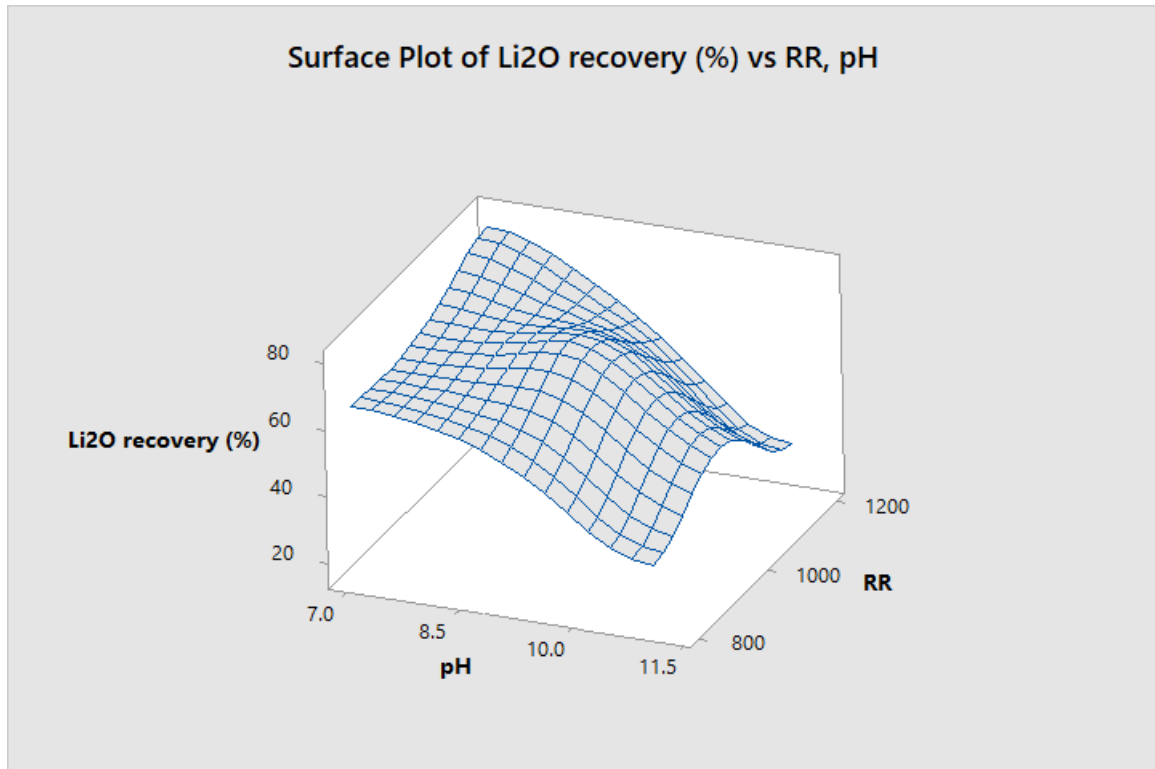


Figure 6-12: Surface plot response for Li₂O recovery by pH vs RR.
Source: Developed by the Minitab 17.

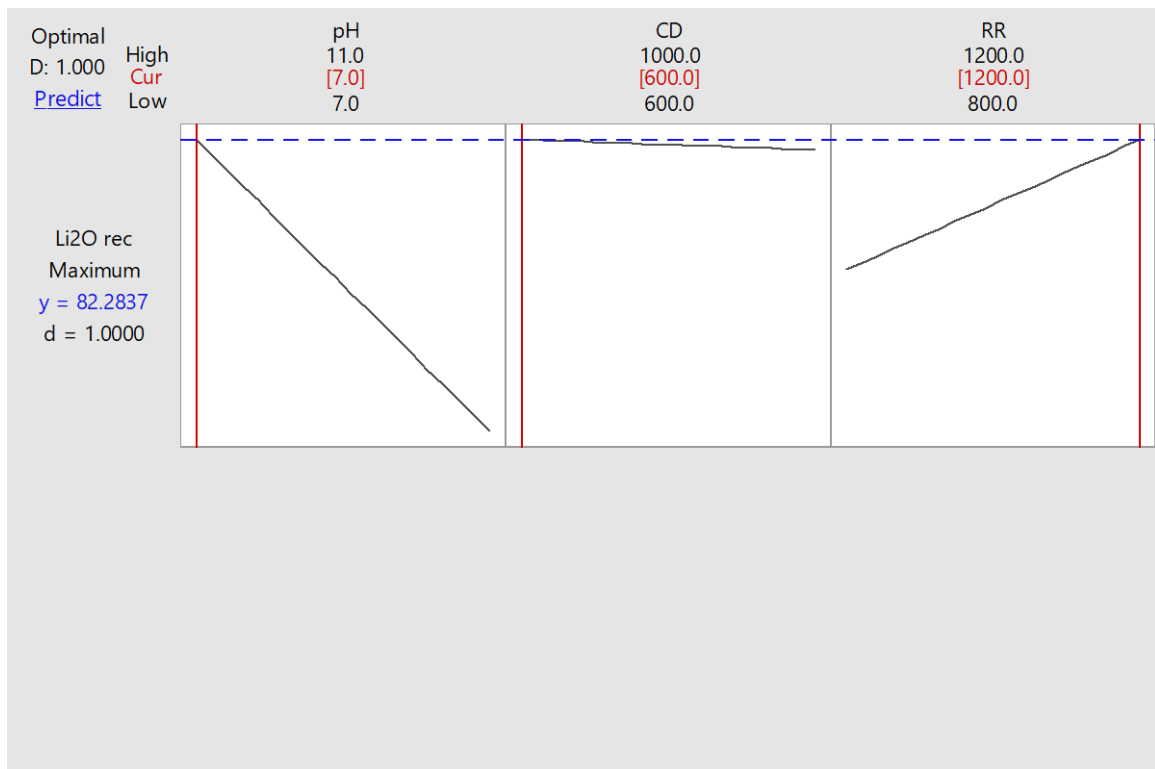


Figure 6-13: Response optimizer for Li₂O recovery.
Source: Developed by the Minitab 17.

Using the Minitab 17 to maximize grade it was found that using pH 7.0, CD 1,000 g/t and RR 800 rpm, a maximum theoretical of 76.58% recovery and 3.49% Li₂O grade can be achieved.

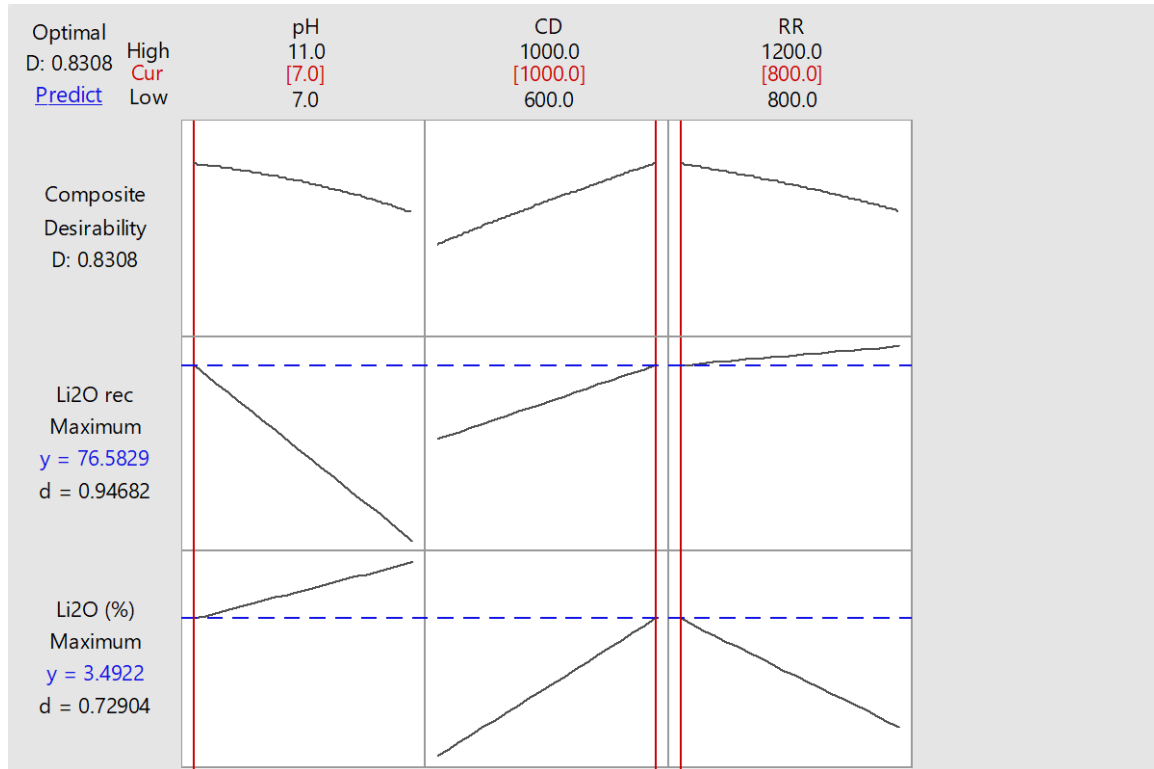


Figure 6-14: Response optimizer for Li₂O grade and recovery.
Source: Developed by the Minitab 17.

COOK and GIBSON (2023) enlighten that for oleate acid at pH 3.6, 6 and 6.2 there are formation of oleate carboxylate anion (RCOO^-), oleate dimer ($[\text{RCOO}]_2^{2-}$) and acid-anion complex ($\text{RCOO}.\text{RCCOH}^-$), respectively, that are responsible for the reduction of the surface tension of the water. Still on that note, around pH 8 spodumene reaches its maximum adsorption by NaOL and equally maximum recovery for microflotation.

After the primary tests it was decided to redo some conditions of interest and explore new ones, the conditions and results are presented in Table 6-4 and Table 6-5, respectively.

Table 6-4: Rougher flotation test parameters.

Test ID	pH	CD	RR
AML-20	7	1000	800
AML-21	11	800	1000
AML-22	7	1000	800
AML-23	11	1000	1000
AML-24	11	1000	1000

Source: Developed by the author.

As shown in the Table 6-5, the maximum Li_2O grade was 5.34% with the lowest recovery of 58.6%, and the largest recovery was 79.95% with a grade of 2.81%.

Table 6-5: Rougher test results.

Test ID	Li_2O		SiO_2		Fe_2O_3		Mass Recovery (%)
	Grade (%)	Recovery (%)	Grade (%)	Recovery (%)	Grade (%)	Recovery (%)	
AML-20	2.76	68.51	68.26	25.37	2.13	61.47	27.87
AML-21	5.34	58.60	63.81	10.19	1.92	25.58	11.70
AML-22	3.01	72.40	69.09	25.69	1.38	54.32	27.72
AML-23*	2.81	79.95	71.27	30.95	1.39	53.23	32.55
AML-24	4.38	68.40	67.30	15.83	1.26	33.51	17.52

Source: Developed by the author.

* - Excessive air flow inlet for a few seconds.'

Comparing the relation of rougher products for Li_2O and Fe_2O_3 , Figure 6-15, it easily shows a trend between the two, as the concentrated lithium oxide increases so those the iron oxide too.

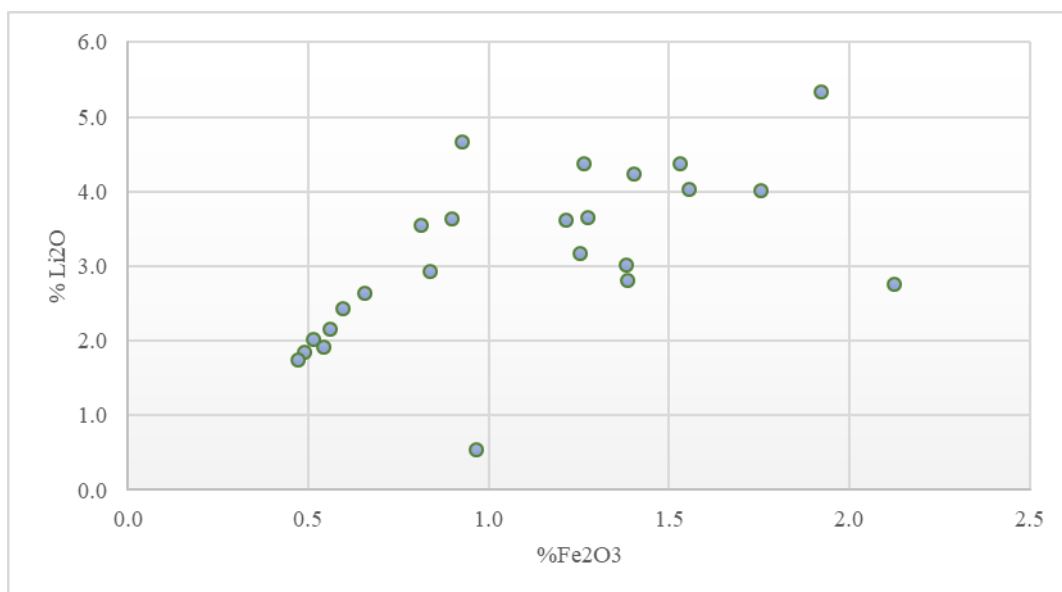


Figure 6-15: Grade comparison for Li_2O and Fe_2O_3 .

Source: Developed by the author.

The presence and direct link between the two were explained by CARDOSO & NEUMANN (2016), explained that minerals that contain lithium in the area aside from spodumene were mica with 0.37% Li and 2.62% Fe and ferro-holmquistite with 1.81% Li and 10.67% Fe. Furthermore, the mica present was described to be muscovite with lithium element substitution in the crystal plane structure. The use of NaOL for iron-bearing minerals has been widely studied and as shown that NaOL adsorptions occurs in iron minerals through chemisorption and electrostatic attraction which leads to a formation of a stable froth layer. At slightly neutral to basic (8–10) pH iron-bearing mineral has the maximum recovery with the use of NaOL as an anionic collector (COOK, GILBSON, 2023; XIE, *et al.*, 2020).

On the other hand, and as expected, for the Li_2O and SiO_2 , Figure 6-16, as the lithium oxide increases the silica decreases to a plateau, about 64%, described in section 1.2.1. COOK & GIBSON (2023) and explains that NaOL can be used as an anionic collector for the flotation of Fe-Al silicates when mixed with DTAC (9:1) cationic collectors exposed to basic conditions.

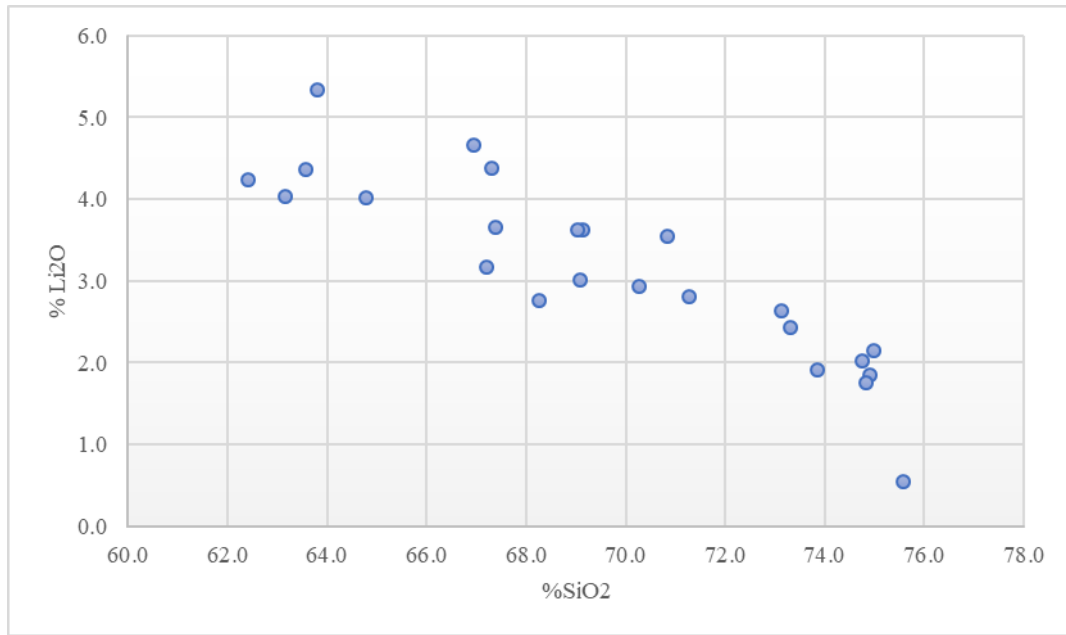


Figure 6-16: Grade comparison for Li_2O and SiO_2 .

Source: Developed by the author.

That conditions for the rougher were then set to be pH 7, CD 600 g/t and RR 1000 rpm, to maximize recovery in this step and maximize grade at the cleaner phase. To guarantee the desired grade it was tested variation of two conditions the pH and collector dosage, on that note, the cleaner test conditions are presented in Table 6-6, all tests' conditions were duplicates.

Table 6-6: Cleaner test conditions.

Test ID	pH	CD (g/t)
AML-25	7	0
AML-26	11	200
AML-27	11	100
AML-28	11	0
AML-29	11	200
AML-30	11	400
AML-31	11	300
AML-32	11	0
AML-33	7	0
AML-34	11	300
AML-35	11	100
AML-36	11	400

Source: Developed by the author.

The outcome of this tests laid-out that maximum Li_2O grade (5.90%) can be achieved when only varying the pH and no additional collector was needed with a mean recovery of 69.34%, with low SiO_2 recovery with average of 30.31% and lowest Fe_2O_3 recovery of 52.61%, overall recovery of lithium oxide of 56.53%. On the other hand, maximum mean recovery, 92.48%, can be through a continuous flotation without pH variation nor additional collector, this simple step had one resulted in the lowest lithium content of average 4.72%, silica of 66.46% and one of the highest iron contents of 1.15% (in average).

Table 6-7: Cleaner test results.

Test ID	Li ₂ O		SiO ₂		Fe ₂ O ₃		Mass Recovery (%)
	Grade (%)	Recovery (%)	Grade (%)	Recovery (%)	Grade (%)	Recovery (%)	
AML-25	4.75	91.86	65.97	61.88	1.27	81.96	64.66
AML-26	5.40	85.25	66.38	46.17	1.04	67.14	48.78
AML-27	5.38	85.22	66.44	41.63	0.95	58.31	44.24
AML-28	5.88	65.65	63.55	26.94	1.29	49.93	30.02
AML-29	5.56	84.57	65.47	43.48	1.02	59.28	46.46
AML-30	5.06	91.75	66.46	51.12	1.01	69.60	53.82
AML-31	5.25	91.77	66.75	55.26	1.00	69.96	57.62
AML-32	5.90	73.03	64.20	33.68	1.12	55.28	37.00
AML-33	4.68	93.09	66.95	56.35	1.03	77.53	59.01
AML-34	5.27	91.51	66.28	54.62	1.01	68.54	57.07
AML-35	5.22	88.43	66.28	46.33	1.04	63.55	46.36
AML-36	4.83	94.20	67.42	54.86	0.95	74.68	57.35

Source: Developed by the author.

To maximize recovery teste AML-25 shows a very interesting approach, where without the need of pH and collector dosage variation there is a significant recovery and grade of Li₂O, with overall 73.23% and 4.75%, respectively. However, this results in one of the highest Fe₂O₃ recovery and grade, 81.96% and 1.27%, respectively, being necessary a third step of dressing for grade achievement.

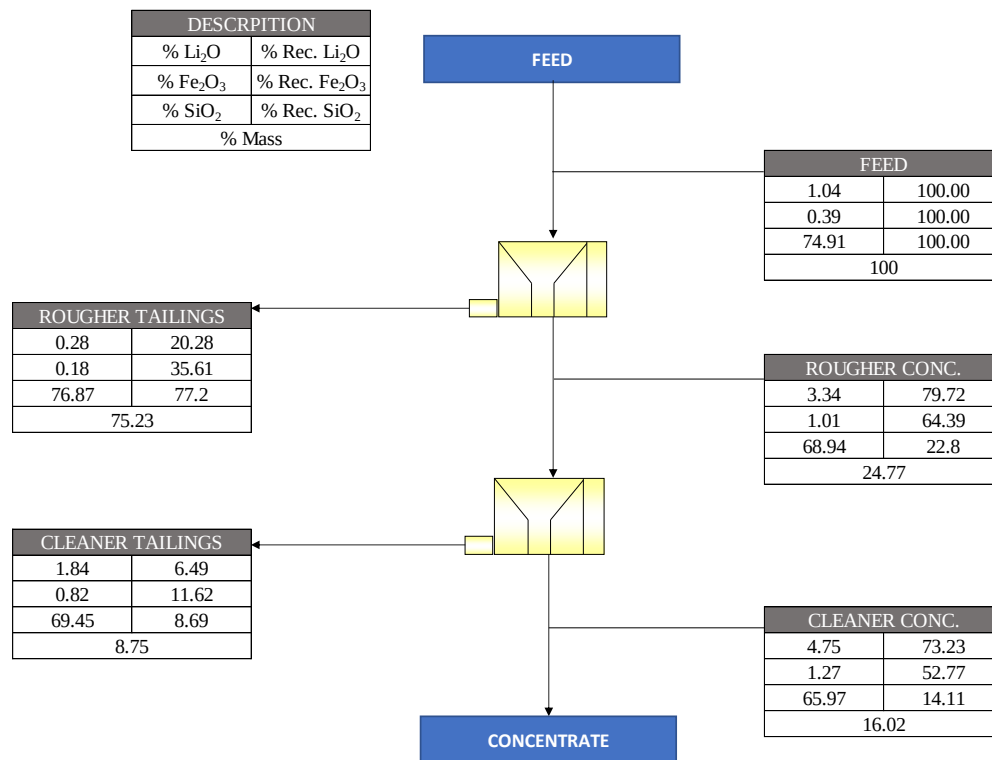


Figure 6-17: Test AML-25 flowsheet results for maximum recovery.

Source: Developed by the author.

In order to obtain a maximum grade, test AML-32 (in Figure 6-18: **Test AML-32 flowsheet results for maximum grade.**) produced 5.90% of lithium oxide but with low recovery of just 60.32%, with iron oxide grade 1.12%, out of specified 0.50% grade. Despite the high Fe₂O₃ content there is a low content in the tailings of 0.53% and high Li₂O of 1.28%, greater than the feed in the rougher step, suggesting an alternative recirculation material for higher material, about 18% of total mass in the process and 22% of total lithium content of the process.

However, there is high grade cleaner tailings in the AML-32 of 1.71% Li₂O that is higher than the feed material suggesting that a recirculation of this tailing material can enrich the process, since it represents about 22.27% of the recovered Li₂O and 18.40% of the mass material.

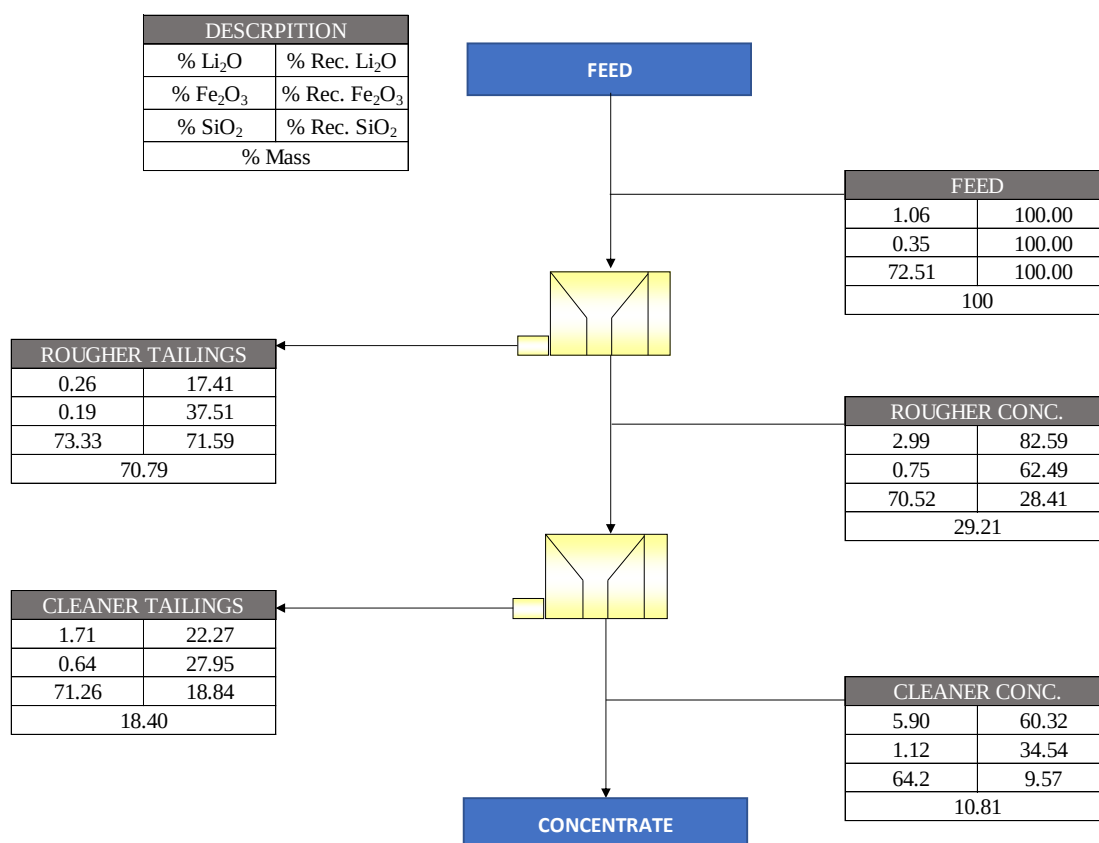


Figure 6-18: Test AML-32 flowsheet results for maximum grade.
Source: Developed by the author.

1.11 FLOTATION OPTIMIZATION

Analysing the results from the industrial and the batch tests, shown in Figure 6-19, the SP 01 with a recovery and grade of Li₂O, with 70,58% and 4.72%, and recovery and grade of Fe₂O₃, 19.05% and 1.05%, respectively, haven't reached market required Li₂O and Fe₂O₃ grades, despite high recovery of Li₂O.

Batch flotation tests showed that with a single stage flotation it is possible to maximising ore grade for test AML-11 reaching 56.02% and 4.66%, Li₂O recovery and grade with 600 g/t of CD, pH 7.0 and 800 rpm for RR, for a balanced medium recovery and grade for AML-09, 77.78% and 2.64% with 600 g/t CD, pH 7.0 and 1.200 rpm RR, and, high recovery for the AML 09, of 78.04% and 1.92% with 1.000 g/t CD, pH 11.0 and 800 rpm RR, respectively.

Despite reaching the minimum market acceptance with AML-11 there is a significant recovery loss, therefore, there is a need for a second stage flotation to guarantee a cleanser Li₂O grade with significant recovery. Using AML-09 as a rougher stage with a reduced RR of 1.000 rpm and without additional CD, AML-25 shows it possible to equal the industrial results with higher Li₂O recovery of 77.65% and 4.75% grade. A better result can be seen from AML-32 where with just variation of pH to 11.0 and no additional CD nor RR variation, it was possible to

achieve 78.95% recovery and 5.90% grade, making this optimized condition for flotation of blend spodumene ore.

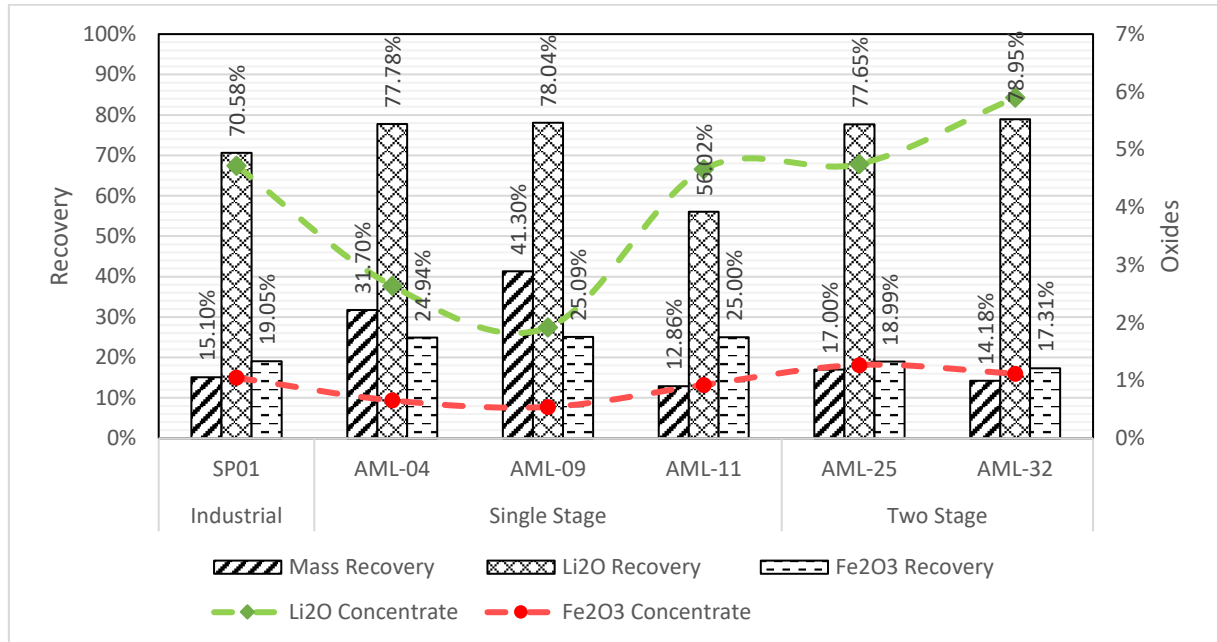


Figure 6-19: Mass, Li₂O and Fe₂O₃ recoveries from industrial, single a two stage flotation.

Source: Developed by the author.

A schematic flowchart of the combined AML-09 and AML-32 tests can be seen in Figure 6-20, where the best combination of two stage (rougher-cleaner) flotation with a stable 1.000 rpm RR in both stages, with addition of 600 g/t of collector and pH 7.0 for the rougher stage and 11.0 for the cleaner stage. The optimal scenario shown in Figure 6-20 requires more tests to better understand the behaviour of the flotation process in this configuration.

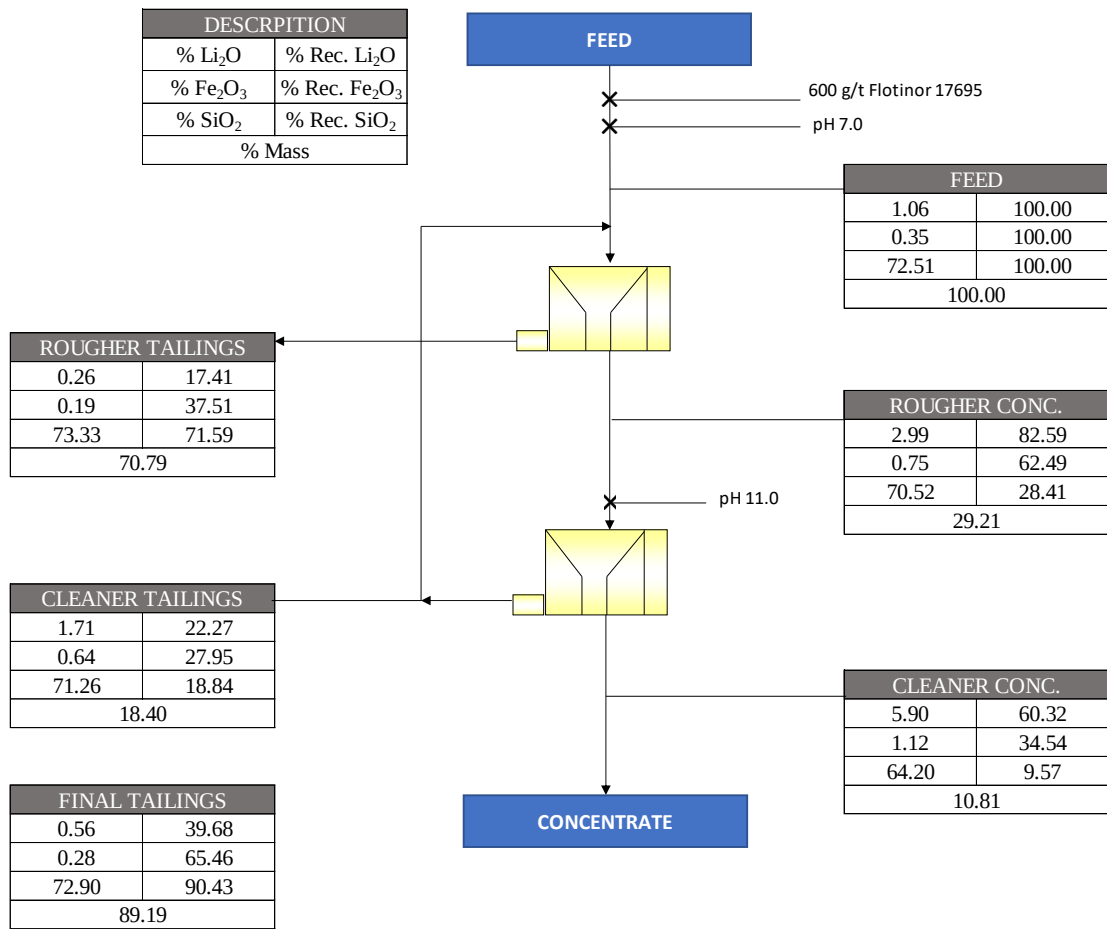


Figure 6-20: Optimized batch flotation test AML-32 with paramaters conditions.
Source: Developed by the author.

7. CONCLUSIONS

With the rise of lithium-ion batteries industry, lithium-bearing minerals have become crucial for the development and growth of the battery industry. Minerals such as specially spodumene and petalite have the highest grade of lithium in their chemical composition, with about 8.02% and 4.90%, respectively.

The biggest lithium producer of lithium 2021 globally was Australian with 52.48% and Brazil contributing with just 1.43%. For global reserves of 2021 Chile had the biggest reserves with 41.03% and Brazil with 0.42%. The main use of lithium globally in 2021 was focused on batteries (74%), followed by production of ceramic and glass (14%).

LIBs are used as cathodes in the battery composition since lithium-base batteries deliver the most storage capacity per unit of space (3.7 V). The mains lithium-base batteries can be composed of NCM (nickel, cobalt, and magnesium), LCO (lithium and cobalt oxide), LFP (lithium, iron and phosphate) and NCA (nickel, cobalt and aluminium). Where, NCA as the highest energy per unit of mass, NCM as good cycle life and classified as promising technology, LFP are classified as very safe, high power however with lower energy density.

Lithium can be extracted from two main sources: brines extraction from underground waters highly concentrated of soluble magnesium, sodium, potassium, iodine, boron, chloride, and lithium chloride, with deposits varying from 0.05% to 0.15% Li. The other source is hard rock form granitic pegmatite rocks, with crystals formed of coarse sizes of a very plural and diverse mineral composition such as quartz, feldspar, micas, lepidolite, columbite-tantalite, muscovite, cassiterite and the main lithium-bearing mineral spodumene. Extraction from hard rock can be accomplish through gravitactic methods such as dense medium separation, spiral concentration and others or for more fineness materials the hydrodynamic method such as direct froth flotation.

Froth flotation of spodumene can be done from direct or reverse flotation, depending on many key factors. The froth flotation can be accomplished by single collectors such as dodecylamine (DDA), sodium oleate (NaOL) and benzohydroxamic acid (BHA), thru mixed collectors such DDA/ NaOL, NaOL/DTAC (dodecyl trimethyl ammonium chloride) and DDA/oxidized paraffin sodium salt. Other commercial collectors such as Flotigram 4343 can also be used for the concentration of spodumene in lithium ores. In this work Flotinor 17695 was used as a cationic fatty acid.

To guarantee efficiency form the forth flotation some conditions must be attended, being the first and mainly the induction hydrophobicity of the interest mineral, the degree of liberation of the interest mineral, the contact between reagent-particle and bubble-particle, the bubble capacity to carry the particles and the separability from the gangue minerals.

The ore used in this work was a blend of tantalum plant reject and tailings dams with a contribution of 50% each. The ore is composed of 11.4% of spodumene, as well as 41.8% albite, 37.2% quartz and other trace minerals such as microcline and muscovite. The ore as a composition of 1.01% of Li_2O , 75.27% SiO_2 , 14.80% Al_2O_3 , 0.37% Fe_2O_3 and other chemical compositions.

The particle size distribution of the feed shows that the top size is about 600 μm and about 70.31% < 150 μm , when compared to the concentrate, about 90.46% and the tailings 67.58%. Through the PSD the Li_2O grade varies very little from 1.18% for the fineness materials (-45 μm) to 1.05% for the coarser material (+150 μm). Past studies clarify that the DOL of spodumene for this ore is about 250 μm . For Fe_2O_3 the same can be seen as the grade increases as the size decreases going from 0.59% to 1.16% with an average of 0.64%.

The use of factorial design using CCD with 3 continuous factors, with 2 replicas per corner points and 3 centre points per 1 block, resulting in 19 runs.

The highest grade achieved AML-11 was of 4.66% grade and 56.03% recovery of Li_2O , 66.96% grade and 8.72% recovery of SiO_2 and 1.28% grade and 22.86% recovery Fe_2O_3 . The conditions used for this run was pH 11.0, 1,000 g/t collector dosage and 800 rpm rotor rotation speed. The maximum recovery AML-13 was about 79.99% with 1.75% grade of Li_2O , 74.83% grade and 48.45% recovery SiO_2 and 0.47% grade and 71.33% recovery of Fe_2O_3 . The conditions used for this run was pH 7.0, 600 g/t collector dosage and 1,200 rpm rotor rotation speed.

For RSM for Li_2O grade concentrate had a coefficient of determination of a R^2 of 81.93%, while for the Li_2O recovery had a coefficient of determination of a R^2 of 73.84%.

To achieved commercial lithium-grade, a cleaner stage was added following primary maximization of the recovery at the rougher stage, for these reasons the rougher stage was defined setting pH 7.0, 600 g/t collector dosage and 1,000 rpm rotor rotation speed. The cleaner flotation shows that it is possible to accomplish a 5.90% grade with 73.03% recovery of Li_2O with just a pH variation of 11.0. Without any variation of pH nor collector dosage it's possible to achieve 92.48% recovery if considering the average of AML-25 and AML-32 but with Li_2O grade of 4.72%.

The best performance for the froth flotation was combining AML-09 changing the rotor rotation speed to 1,000, combined with AML-32 shifting pH from 7.0 to 11.0. As a result, it is expected a grade of 5.90% Li_2O with a 10.81% mass and global recovery of 78.95%. in this scenario, the Fe_2O_3 grade is 1.27% higher than commercial specification, with a global recovery of 62.74% and SiO_2 grade of 63.05%, close to pure spodumene silica grade, with a global recovery of 15.84%.

Optimize conditions suggest a froth flotation of spodumene with two-step flotation, rougher and cleaner stages with a recirculation of the cleaner tailings mixing and feeding the rougher stage to minimize recovery loss.

8. CONCLUSÃO

Com o crescimento da indústria das baterias de íon-lítio, os minerais que contêm lítio tornaram-se cruciais para o desenvolvimento e crescimento da indústria de baterias. Minerais como, especialmente, espodumênio e petalita têm o maior teor de lítio em sua composição química, com cerca de 8,02% e 4,90%, respectivamente.

O maior produtor de lítio em 2021 globalmente foi a Austrália, com 52,48%, enquanto o Brasil contribuiu com apenas 1,43%. Em relação às reservas globais de 2021, o Chile possuía as maiores reservas, com 41,03%, e o Brasil com 0,42%. O principal uso do lítio globalmente em 2021 foi focado em baterias (74%), seguido pela produção de cerâmica e vidro (14%).

As baterias de íon-lítio (LIBs) são usadas como cátodos na composição das baterias, uma vez que as baterias à base de lítio oferecem a maior capacidade de armazenamento por unidade de espaço (3,7 V). As principais baterias à base de lítio podem ser compostas por NCM (níquel, cobalto e manganês), LCO (lítio e óxido de cobalto), LFP (lítio, ferro e fosfato) e NCA (níquel, cobalto e alumínio). Entre elas, a NCA possui a maior energia por unidade de massa, a NCM tem boa vida útil de ciclo e é considerada uma tecnologia promissora, enquanto as LFP são classificadas como muito seguras, de alta potência, porém com menor densidade de energia.

O lítio pode ser extraído de duas fontes principais: salmouras extraídas de águas subterrâneas altamente concentradas de elementos solúveis como o magnésio, sódio, potássio, iodo, boro, cloreto e cloreto de lítio, com depósitos variando de 0,05% a 0,15% de Li. A outra fonte é a rocha dura, formada por rochas pegmatíticas graníticas, com cristais de tamanho grosso e composição mineral muito diversa, como quartzo, feldspato, micas, lepidolita, columbita-tantalita, muscovita, cassiterita e o principal mineral que contém lítio, espodumênio. A extração de rocha dura pode ser realizada por métodos gravimétricos, como separação em meio denso, concentração em espiral e outros, ou, para materiais mais finos, o método hidrodinâmico, como a flotação.

A flotação de espodumênio pode ser realizada por flotação direta ou reversa, dependendo de muitos de fatores chave. A flotação pode ser realizada por coletores únicos, como dodecilamina (DDA), oleato de sódio (NaOL) e ácido benzohidroxâmico (BHA), ou por coletores mistos, como DDA/NaOL, NaOL/DTAC (cloreto de dodecil trimetil amônio) e DDA/sal de parafina oxidada. Outros coletores comerciais, como Flotigram 4343, também podem ser usados para a concentração de espodumênio em minérios de lítio. Neste trabalho, foi utilizado o Flotinor 17695 como um ácido graxo catiônico.

Para garantir a eficiência da flotação, algumas condições devem ser atendidas, sendo a primeira e principal a indução da hidrofobicidade no mineral de interesse, o grau de liberação do mineral de interesse, o contato entre reagente-partícula e bolha-partícula, a capacidade da bolha de transportar as partículas e a separabilidade dos minerais de ganga.

O minério utilizado neste trabalho foi uma mistura de rejeito de planta de tântalo e rejeitos de barragens, com contribuição de 50% cada. O minério é composto por 11,4% de espodumênio, assim como 41,8% de albita, 37,2% de quartzo e outros minerais traços, como microclina e muscovita. O minério tem uma composição de 1,01% de Li_2O , 75,27% de SiO_2 , 14,80% de Al_2O_3 , 0,37% de Fe_2O_3 e outras composições químicas.

A distribuição de tamanho de partícula da alimentação mostra que o tamanho máximo é cerca de 600 μm e cerca de 70,31% < 150 μm , quando comparado ao concentrado, cerca de 90,46% e os rejeitos 67,58%. O teor de Li_2O varia muito pouco em função da granulometria, de 1,18% para os materiais mais finos (-45 μm) a 1,05% para o material mais grosso (+150 μm). Estudos anteriores clarificam que o GL do espodumênio para este minério é cerca de 250 μm . Para o Fe_2O_3 , pode-se observar que o teor aumenta à medida que o tamanho diminui, indo de 0,59% a 1,16%, com uma média de 0,64%.

O uso de planejamento fatorial usando composto central (CCD) com 3 fatores contínuos, com 2 réplicas por pontos de canto e 3 pontos centrais por 1 bloco, resultando em 19 testes.

O maior teor alcançado, AML-11, foi de 4,66% de teor e 56,03% de recuperação de Li_2O , 66,96% de teor e 8,72% de recuperação de SiO_2 e 1,28% de teor e 22,86% de recuperação de Fe_2O_3 . As condições utilizadas para esta execução foram pH 11,0, dosagem de coletor de 1.000 g/t e velocidade de rotação do rotor de 800 rpm. A máxima recuperação, AML-13, foi de cerca de 79,99% com 1,75% de teor de Li_2O , 74,83% de teor e 48,45% de recuperação de SiO_2 e 0,47% de teor e 71,33% de recuperação de Fe_2O_3 . As condições utilizadas para esta execução foram pH 7,0, dosagem de coletor de 600 g/t e velocidade de rotação do rotor de 1.200 rpm.

Usando o método de superfície de resposta (RSM), o teor de Li_2O no concentrado teve um coeficiente de determinação de R^2 de 81,93%, enquanto para a recuperação de Li_2O teve um coeficiente de determinação de R^2 de 73,84%.

Para alcançar um teor comercial de lítio, uma etapa de limpeza foi adicionada após a maximização primária da recuperação na etapa rougher. Por essas razões, a etapa rougher foi definida com pH 7,0, dosagem de coletor de 600 g/t e velocidade de rotação do rotor de 1.000 rpm. A flotação de limpeza mostrou que é possível alcançar um teor de 5,90% com 73,03% de recuperação de Li_2O apenas com uma variação de pH de 11,0. Sem qualquer variação de pH nem de dosagem de coletor, é possível alcançar 92,48% de recuperação, considerando a média de AML-25 e AML-32, mas com um teor de Li_2O de 4,72%.

O melhor desempenho para a flotação foi combinando AML-09, mudando a velocidade de rotação do rotor para 1.000, combinada com AML-32, alterando o pH de 7,0 para 11,0. Como resultado, espera-se um teor de 5,90% de Li_2O com 10,81% de massa e recuperação global de 78,95%. Neste cenário, o teor de Fe_2O_3 é 1,27% maior que a especificação comercial, com recuperação global de 62,74% e teor de SiO_2 de 63,05%, próximo ao teor de sílica de espodumênio puro, com recuperação global de 15,84%.

As condições otimizadas sugerem uma flotação de espodumênio em duas etapas, rougher e cleaner, com recirculação dos rejeitos da cleaner misturando e alimentando a etapa rougher para minimizar a perda de recuperação.

9. FUTURE WORKS

- Realize mineral characterization through Mineral Liberation Analysis (MLA).
- Determine presence of Fe-bearing minerals distribution and Fe sites on the silicates along the blend ore.
- Realize more analysis to determine the DOL of the blended ore.
- Realize third-stage cleaner the evaluate the conditions used in test AML-09.
- Realize bench scale tests with recirculation of rejected material from the cleaner stage.
- Analysis the influence of the slurry ions on the recirculation material.
- Realize pilot scale tests on the optimized conditions.
- Evaluate the use of a magnetic separation prior and/or after flotation process.
- Evaluate the regrinding of the rougher rejects and scavenger flotation to increase recovery.
- Evaluate the flotation of more fineness material ($-38\text{ }\mu\text{m}$).

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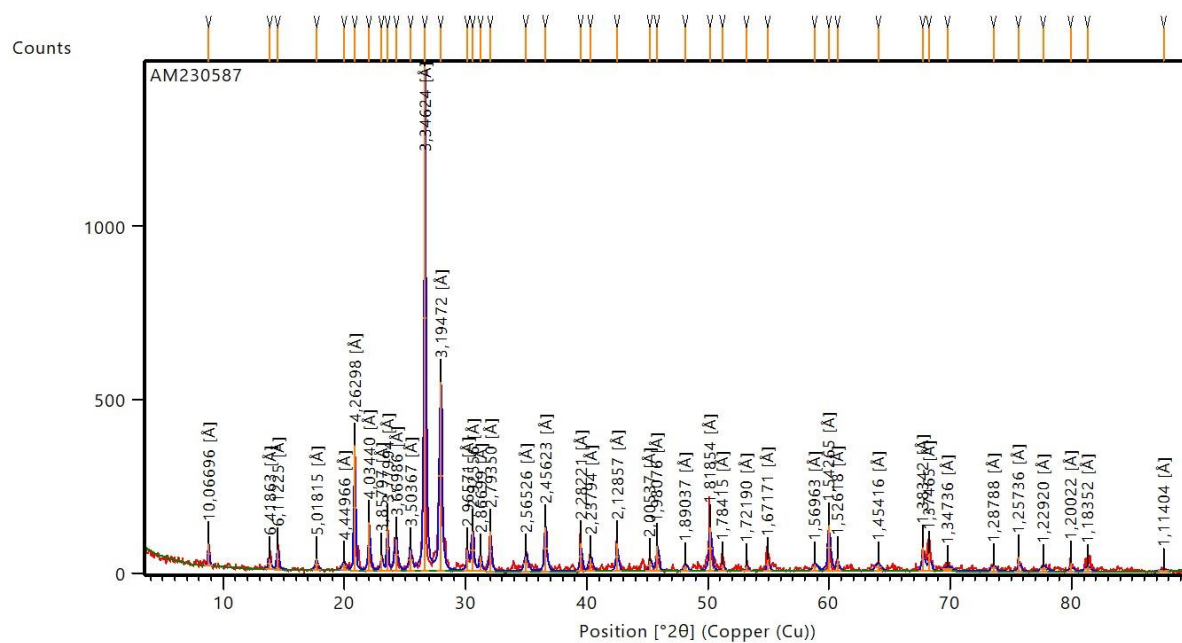
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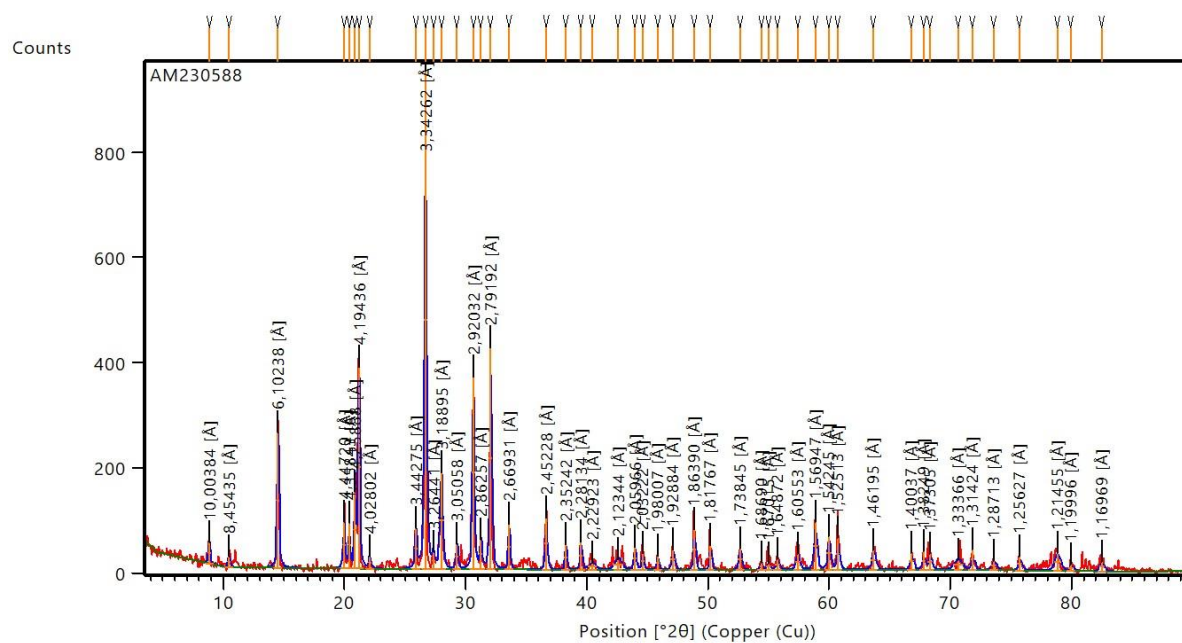
11. APPENDIX

1.12 X-RAY DIFFRACTION (XRD)

1.12.1 Feed



1.12.2 Concentrate



1.12.3 Tailings

1.13.3 Tailings

INITIAL MASS (g)	SIZE (µm)	RETAINED (g)	RETAINED CORRECTED (g)	% RETRAINED	% ACCUMULATED RETAINED	% ACCUMULATED PASSING	RR	Erro ²
132.3	600	0.00	0.00	0.00	0.00	100.00	100.00	0.00
	425	0.40	0.40	0.30	0.30	99.70	99.99	0.09
	300	2.30	2.31	1.75	2.05	97.95	98.75	0.63
	212	18.40	18.48	13.97	16.02	83.98	87.71	13.91
	150	21.60	21.70	16.40	32.42	67.58	63.44	17.15
	106	41.10	41.29	31.21	63.63	36.37	38.22	3.43
	75	18.20	18.28	13.82	77.45	22.55	20.64	3.66
	53	16.80	16.88	12.76	90.21	9.79	10.47	0.46
	38	12.30	12.36	9.34	99.54	0.46	5.32	23.62
	0	0.60	0.60	0.46	100.00	0	0.00	0.00
	131.700				k		125.8425	62.95231
				0	m		2.121882	

1.14 COLLECTOR DOSAGE IN MASS AND VOLUME CALCULATION

Collector Dosage (g/t)	Collector dosage in mass (g)	Concentration (% p/v)	Volume (mL)
100	0.05	1%	5
200	0.1		10
600	0.3		30
800	0.4		40
1000	0.5		50

1.15 FLOTATION TESTS

1.15.1 Design of experiments trials runs

StdOrder	RunOrder	CenterPt	Blocks	A	B	C	pH	Coletor (g/t)	Rotação rotor (rpm)
17	1	0	1	0	0	0	9	800	1000
3	2	1	1	-1	1	-1	7	1000	800
6	3	1	1	1	-1	1	11	600	1200
1	4	1	1	-1	-1	-1	7	600	800
9	5	1	1	-1	-1	-1	7	600	800
16	6	1	1	1	1	1	11	1000	1200
15	7	1	1	-1	1	1	7	1000	1200
7	8	1	1	-1	1	1	7	1000	1200
5	9	1	1	-1	-1	1	7	600	1200
14	10	1	1	1	-1	1	11	600	1200
12	11	1	1	1	1	-1	11	1000	800
10	12	1	1	1	-1	-1	11	600	800
13	13	1	1	-1	-1	1	7	600	1200
8	14	1	1	1	1	1	11	1000	1200
2	15	1	1	1	-1	-1	11	600	800
4	16	1	1	1	1	-1	11	1000	800
11	17	1	1	-1	1	-1	7	1000	800
18	18	0	1	0	0	0	9	800	1000
19	19	0	1	0	0	0	9	800	1000

1.15.2 Rougher tests mass results

Flotação Rougher								
Concentration	1% p/v	Conditioning time	2min	Conditioning rotation	1000 rpm			
		Flotation time	3min	Flotation rotation	Depending on			
Test ID	pH	Dosage (g/t)	Rotor rotation (rpm)	Feed mass (g)	Concentrate mass (g)	Tailings mass (g)	Feed recalculated (g)	Mass loss (%)
AML-01	9	800	1000	500.01	124.61	372.84	497.45	0.51
AML-02	7	1000	800	500.07	99.08	397.62	496.7	0.67
AML-03	11	600	1200	500.27	36.17	459.39	495.56	0.94
AML-04	7	600	800	500.08	157.75	339.71	497.46	0.52
AML-05	7	600	800	500.6	137.95	358.38	496.33	0.85
AML-06	11	1000	1200	500.19	37.42	459.13	496.55	0.73
AML-07	7	1000	1200	500.74	218.88	277.84	496.72	0.80
AML-08	7	1000	1200	500.08	197.87	290.68	488.55	2.31
AML-09*	7	600	1200	500.4	205.42	291.79	497.21	0.64
AML-10	11	600	1200	500.16	47.11	448.87	495.98	0.84
AML-11	11	1000	800	500.15	63.71	431.51	495.22	0.99
AML-12	11	600	800	500.05	29.16	466.78	495.94	0.82
AML-13	7	600	1200	500.04	238.05	254.25	492.3	1.55
AML-14	11	1000	1200	500.19	37.12	456.62	493.74	1.29
AML-15	11	600	800	500.72	21.85	473.21	495.06	1.13
AML-16	11	1000	800	500.03	19.92	475.47	495.39	0.93
AML-17	7	1000	800	500.33	113.64	380.91	494.55	1.16
AML-18	9	800	1000	500.43	179.92	313.54	493.46	1.39
AML-19	9	800	1000	500.14	160.67	335.07	495.74	0.88
AML-20	7	1000	800	500.72	138.16	357.63	495.79	0.98
AML-21	11	800	1000	500.25	57.24	431.87	489.11	2.23
AML-22	7	1000	800	500.69	136.93	357.12	494.05	1.33
AML-23*	11	1000	1000	500.17	160.53	332.70	493.23	1.39
AML-24	11	1000	1000	500.46	86.24	405.88	492.12	1.67

* - excesso de aeracao durante 15s

1.15.3 Cleaner tests mass results

Flotation tests													
ROUGHER						CLEANER							
Conditioning time	2min	Rotation (rpm)	1000 rpm			Conditioning time	1min	Rotation (rpm)		1000 rpm			
Flotation time	3min		WEIGHT MASS (g)			Flotation time	3min		WEIGHT MASS (g)				
Test ID	pH	Dosage (g/t)	Feed	Tailings 1	Feed recalculated	pH	Dosage (g/t)	Concentrate recalculated 1	Mass Recovery 1 (%)	Tailings 2	Concentrate 2	Mass Recovery 2 (%)	Mass loss (%)
AML-25	7	600	505.78	373.41	496.36	7	0	122.95	24.77063111	43.45	79.50	64.66	1.86
AML-26	7	600	503.85	344.19	495.95	11	200	151.76	30.60013872	77.73	74.03	48.78	1.57
AML-27	7	600	504.68	340.73	496.95	11	100	156.22	31.43562015	87.11	69.11	44.24	1.53
AML-28	7	600	501.44	334.20	491.65	11	0	157.45	32.02467614	110.18	47.27	30.02	1.95
AML-29	7	600	500.18	346.38	480.55	11	200	134.17	27.91994157	71.84	62.33	46.46	3.92
AML-30	7	600	500.08	347.70	490.42	11	400	142.72	29.10144183	65.91	76.81	53.82	1.93
AML-31	7	600	501.11	363.43	494.79	11	300	131.35	26.54758512	55.66	75.69	57.62	1.26
AML-32	7	600	500.73	348.19	491.86	11	0	143.67	29.20953117	90.51	53.16	37.00	1.77
AML-33	7	600	502.06	351.89	495.50	7	0	143.61	28.98284561	58.86	84.75	59.01	1.31
AML-34	7	600	500.63	365.96	491.90	11	300	125.94	25.60276479	54.06	71.88	57.07	1.74
AML-35	7	600	503.04	335.99	493.76	11	100	157.77	31.95277058	84.63	73.14	46.36	1.84
AML-36	7	600	500.63	348.67	491.63	11	400	142.96	29.07877876	60.97	81.99	57.35	1.80

1.15.4 Chemical tests results

OBS	SiO2 (%)	Al2O3 (%)	Fe2O3 (%)	HA2O (%)	K2O (%)	CAO (%)	MGO (%)	MNO (%)	P2O5 (%)	TiO2 (%)	TA2O5 (PPM)	HB2O5 (PPI)	SN (PPI)	Li2O (%)	RB2O-ICP (PPI)
AML 01 - AF	75.81	14.11	0.24	5.13	2.21	0.15	0.02	0.11	0.04	<0.01	85.42	25.97	60.57	0.44	0.75
AML 01 - FL	70.28	16.98	0.84	3.45	1.20	1.37	0.31	0.11	0.34	0.15	311.04	45.06	424.24	2.93	0.31
AML 02 - AF	75.59	13.48	0.23	5.35	2.14	0.17	0.07	0.11	0.06	<0.01	66.96	26.01	49.58	0.36	0.69
AML 02 - FL	69.13	19.76	0.90	2.60	1.02	1.54	0.32	0.12	0.34	0.18	430.62	56.42	480.17	3.63	0.22
AML 03 - AF	75.29	14.63	0.27	4.54	2.06	0.20	0.05	0.11	0.05	<0.01	120.63	29.64	87.74	0.80	0.55
AML 03 - FL	64.78	20.49	1.75	2.11	0.86	4.03	0.64	0.15	0.95	0.37	251.88	38.53	643.98	4.02	0.24
AML 04 - AF	76.35	13.57	0.25	4.97	2.18	0.17	0.03	0.11	0.05	<0.01	62.76	26.57	66.92	0.35	0.75
AML 04 - FL	73.13	18.32	0.66	3.66	1.25	1.15	0.26	0.10	0.25	0.13	237.98	44.75	271.79	2.64	0.31
AML 05 - AF	75.99	13.83	0.27	5.19	2.20	0.17	0.07	0.11	0.05	<0.01	69.41	25.11	50.27	0.35	0.76
AML 05 - FL	75.57	13.65	0.97	4.67	1.56	1.01	0.34	0.11	0.11	0.09	81.18	30.32	144.15	0.54	0.48
AML 06 - AF	75.88	14.12	0.31	4.82	1.99	0.22	0.07	0.11	0.05	<0.01	108.32	32.53	109.38	0.86	0.57
AML 06 - FL	69.04	24.81	1.21	2.76	0.79	3.46	0.65	0.14	1.27	0.40	196.86	44.20	447.77	3.62	0.18
AML 07 - AF	75.09	14.21	0.28	4.68	2.43	0.16	0.05	0.14	0.05	<0.01	62.55	25.38	47.91	0.42	0.91
AML 07 - FL	74.91	16.11	0.49	4.27	1.20	0.88	0.19	0.08	0.20	0.08	180.95	39.15	217.32	1.85	0.23
AML 08 - AF	74.90	13.58	0.26	4.87	2.39	0.19	0.05	0.13	0.07	<0.01	70.37	28.08	84.28	0.41	0.87
AML 08 - FL	74.74	16.88	0.52	4.55	1.18	0.96	0.20	0.08	0.19	0.10	178.27	38.01	246.36	2.02	0.23
AML 09 - AF	75.69	13.83	0.26	4.53	2.33	0.15	0.04	0.13	0.05	<0.01	70.98	24.30	53.60	0.38	0.84
AML 09 - FL	73.86	16.16	0.54	3.93	1.36	0.84	0.19	0.09	0.18	0.10	269.63	40.36	249.56	1.92	0.27
AML 10 - AF	75.41	14.06	0.28	4.57	2.02	0.21	0.06	0.11	0.05	<0.01	105.10	27.37	63.49	0.77	0.53
AML 10 - FL	67.37	19.31	1.28	2.53	0.88	2.90	0.41	0.13	0.68	0.29	255.06	42.79	571.76	3.66	0.24
AML 11 - AF	75.71	13.89	0.28	5.06	2.09	0.22	0.06	0.11	0.05	<0.01	72.53	26.36	88.19	0.54	0.72
AML 11 - FL	66.96	21.14	0.93	1.79	0.63	2.01	0.22	0.13	0.50	0.21	400.33	54.32	578.73	4.72	0.15
AML 12 - AF	75.10	14.69	0.30	4.58	2.05	0.24	0.07	0.11	0.05	<0.01	107.08	28.56	99.45	0.80	0.52
AML 12 - FL	63.58	21.20	1.53	1.57	0.74	3.85	0.40	0.17	1.07	0.33	318.80	47.50	605.40	4.37	0.22
AML 13 - AF	74.65	14.68	0.27	4.77	2.55	0.14	0.04	0.13	0.05	<0.01	70.05	28.95	78.60	0.41	0.93
AML 13 - FL	74.83	16.21	0.47	4.42	1.31	0.83	0.18	0.08	0.19	0.07	152.90	36.12	186.74	1.75	0.27
AML 14 - AF	75.40	14.62	0.29	4.86	2.02	0.22	0.07	0.11	0.05	<0.01	111.72	29.23	91.38	0.87	0.52
AML 14 - FL	67.21	18.79	1.25	2.84	0.95	3.23	0.35	0.14	0.84	0.29	227.72	39.33	470.80	3.17	0.25
AML 15 - AF	75.49	15.58	0.32	4.35	2.15	0.26	0.10	0.11	0.04	0.04	139.38	29.07	74.99	0.41	0.87
AML 15 - FL	63.15	20.62	1.56	1.89	0.77	4.75	0.41	0.17	1.35	0.36	283.36	41.42	571.89	4.03	0.22
AML 16 - AF	75.31	14.62	0.33	4.54	1.98	0.29	0.08	0.11	0.06	0.00	120.18	30.94	113.75	0.92	0.55
AML 16 - FL	62.41	21.22	1.40	1.62	0.68	4.57	0.20	0.17	1.31	0.30	254.23	37.09	511.05	4.23	0.18
AML 17 - AF	76.74	13.36	0.24	5.01	2.14	0.16	0.02	0.11	0.04	<0.01	50.57	25.34	56.30	0.35	0.77
AML 17 - FL	70.83	21.25	0.81	3.09	1.00	1.56	0.44	0.11	0.38	0.19	298.10	50.34	376.45	3.54	0.23
AML 18 - AF	74.69	13.83	0.29	5.06	2.35	0.17	0.05	0.13	0.06	<0.01	75.79	25.14	77.74	0.47	0.86
AML 18 - FL	74.99	17.09	0.56	4.11	1.08	1.05	0.22	0.08	0.20	0.11	188.82	38.85	224.93	2.15	0.22
AML 19 - AF	76.19	13.73	0.26	4.91	2.26	0.14	0.02	0.12	0.04	<0.01	78.19	26.98	58.51	0.43	0.82
AML 19 - FL	73.30	17.01	0.60	3.79	1.14	1.21	0.29	0.09	0.36	0.13	189.34	44.47	297.80	2.43	0.27
AML20 - AF	77.22	13.28	0.58	4.60	1.75	0.18	0.05	0.10	0.03	0.02	<0.01	99.47	<0.01	0.49	0.61
AML 20 - FL	68.26	16.73	2.13	2.88	0.40	1.18	0.16	0.13	0.21	0.02	<0.01	488.67	<0.01	2.76	0.40
AML 21 - AF	76.49	13.24	0.53	4.55	1.64	0.22	0.05	0.11	0.04	0.02	<0.01	153.96	<0.01	0.50	0.57
AML 21 - FL	63.81	22.98	1.92	1.18	0.29	2.40	0.32	0.14	0.47	0.15	<0.01	244.80	<0.01	5.34	0.08
AML 22 - AF	76.35	12.62	0.48	4.31	1.72	0.22	0.09	0.11	0.05	0.02	4.25	94.92	<0.01	0.44	0.57
AML 22 - FL	69.09	17.72	1.38	2.84	0.77	1.16	0.18	0.13	0.23	0.07	<0.01	317.16	<0.01	3.01	0.35
AML 23 - AF	76.16	12.56	0.67	4.89	2.18	0.15	0.01	0.11	0.04	<0.01	60.97	222.80	60.73	0.34	0.63
AML 23 - FL	71.27	17.15	1.39	2.99	0.78	1.10	0.19	0.10	0.21	0.08	<0.01	251.86	<0.01	2.81	0.27
AML 24 - AF	76.91	12.81	0.46	4.60	1.82	0.19	0.05	0.11	0.04	0.02	25.39	86.75	<0.01	0.43	0.62
AML 24 - FL	67.30	19.61	1.26	2.28	0.72	1.53	0.20	0.14	0.34	0.14	164.01	131.84	68.45	4.38	0.19
AML 25 FL 2	65.97	21.36	1.27	1.62	0.86	1.80	0.29	0.13	0.42	0.21	570.19	59.79	610.40	4.75	0.17
AML 25 - AF 1	76.88	13.10	0.18	5.39	2.00	1.69	0.26	0.13	0.40	0.20	34.43	24.67	565.35	0.28	0.15
AML 25 - AF 2	74.35	15.10	0.51	4.95	2.15	1.90	0.25	0.13	0.44	0.22	91.01	28.08	633.22	0.77	0.13
AML 26 - FL 2	66.38	21.52	1.04	1.27	0.46	0.15	0.04	0.11	0.05	0.01	575.71	65.32	66.59	5.40	0.58
AML 26 - AF 1	73.94	14.84	0.48	5.09	2.32	2.35	0.25	0.14	0.60	0.26	108.44	28.13	830.47	0.57	0.09
AML 26 - AF 2	73.73	15.05	0.48	5.14	2.35	0.18	0.06	0.10	0.04	0.01	105.38	28.23	36.94	0.89	0.57
AML 27 - FL 2	66.44	21.39	0.95	1.28	0.40	0.16	0.03	0.10	0.04	0.01	529.00	62.92	42.88	5.38	0.57
AML 27 - AF 1	77.34	12.92	0.18	5.14	1.99	0.34	0.20	0.11	0.05	0.03	45.78	24.15	53.64	0.28	0.61
AML 27 - AF 2	73.88	15.19	0.54	4.93	2.26	0.34	0.17	0.11	0.05	0.03	153.20	32.42	90.90	0.74	0.59
AML 28 - FL 2	63.55	23.36	1.29	0.84	0.37	0.15	0.04	0.10	0.04	0.01	691.97	75.15	42.58	5.88	0.59
AML 28 - AF 1	76.94	13.18	0.19	5.15	2.06	0.34	0.15	0.11	0.06	0.03	35.65	24.53	62.14	0.31	0.56
AML 28 - AF 2	73.94	15.96	0.56	4.53	1.88	0.26	0.11	0.11	0.04	0.02	113.89	29.36	44.75	1.32	0.64
AML 29 - FL 2	65.47	22.46	1.02	1.14	0.38	0.28	0.14	0.10	0.05	0.02	551.00	65.41	38.75	5.56	0.54
AML 29 - AF 1	76.58	13.67	0.21	5.15	2.06	0.15	0.02	0.10	0.04	0.01	49.52	23.35	50.55	0.32	0.47
AML 29 - AF 2	73.84	15.49	0.61	4.89	2.16	0.43	0.17	0.11	0.05	0.05	161.98	31.79	105.75	0.88	0.46
AML 30 - FL 2	66.46	21.24	1.01	1.50	0.52	0.28	0.13	0.10	0.05	0.02	550.62	64.74	69.13	5.06	0.56
AML 30 - AF 1	77.22	13.13	0.19	5.04	2.03	2.51	0.26	0.15	0.65	0.26	58.51	23.91	829.78	0.31	0.10
AML 30 - AF 2	74.07	15.06	0.52	4.97	2.13	0.31	0.15	0.11	0.05	0.03	115.92	28.34	77.75	0.53	0.63
AML 31 - FL 2	66.75	21.34	1.00	1.40	0.47	1.82	0.23	0.13	0.42	0.22	563.92	65.36	640.59	5.25	0.11
AML 34 - AF 1	73.18	15.08	0.62	5.07	2.38	1.86	0.28	0.14	0.45	0.21	110.52	27.91	619.84	0.59	0.14
AML 31 - AF 1	73.22	15.47	0.59	5.05	2.42	0.32	0.16	0.11	0.06	0.03	106.73	27.05	81.34	0.62	0.75
AML 31 - AF 2	73.48	15.59	0.58	5.01	2.40	0.25	0.12	0.11	0.05	0.02	100.95	26.37	68.92	0.64	0.61
AML 32 - FL 2	64.20	23.23	1.12	0.81	0.35	0.34	0.18	0.11	0.05	0.03	655.43	74.40	61.22	5.90	0.62
AML 32 - AF 1	73.32	13.39	0.19	5.37	2.35	0.41	0.18	0.10	0.05	0.04	49.95	24.22	101.04	0.26	0.46
AML 32 - AF 2	74.24	20.70	0.53	4.71	1.86	0.35	0.20	0.11	0.06	0.03	147.36	32.22	83.72	1.28	0.62
AML 33 - FL 2	66.95	25.91	1.03	1.68	0.65	0.35	0.21	0.11	0.06	0.03	551.83	64.94	80.89	4.68	0.63
AML 33 - AF 1	74.80	14.41	0.43	5.35	2.21	0.15	0.09	0.11	0.06	0.01	63.65	24.91	74.11	0.46	0.59
AML 33 - AF 2	74.68	14.68	0.43	5.23	2.21	0.15	0.02	0.10	0.04	0.01	70.59	22.41	51.84	0.50	0.59
AML 34 - FL 2	66.28	22.32	1.01	1.29	0.47	2.09	0.2								