

Review

A Review of Fatty Acid Collectors: Implications for Spodumene Flotation

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Abstract: Increasing demand for lithium-ion batteries has led to the development of several new lithium mineral projects around the globe. Some major mineral processing challenges these projects face are similarities in gangue and value mineral behaviour and poor selectivity in froth flotation. Unsaturated anionic fatty acids are the primary spodumene flotation collectors, known to be strong collectors with poor solubility and selectivity. Fundamental flotation research consensus is that spodumene flotation is driven by a fatty acid–anion complex adsorbed at cationic aluminum sites. However, many small-scale studies result in poor recoveries, prompting several researchers to investigate cationic activators or mixed anionic/cationic collectors to improve flotation performance. Testwork with real spodumene ore is rare in recent literature, but older publications from several deposits prove that fatty acids can successfully concentrate spodumene. The process generally includes alkaline scrubbing, high-density fatty acid conditioning, and flotation at pH 7.5–8.5 with 500–750 g/t fatty acid collector. The collector speciation behaviour is notably sensitive to pulp conditions around this pH; possibly resulting in unstable flotation circuits and inconsistent results. This paper reviews fatty acid collector properties and the available industrial and fundamental spodumene flotation research. We aim to provide new insight for understanding particle-collector interactions in spodumene flotation and help bridge the gap between fundamental and industrial processes which will be needed to de-risk projects in the growing lithium mineral industry.

Keywords: spodumene; lithium; flotation; fatty acids; collectors; oleic acid; tall oil



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1. Introduction

There is a pressing need for the mining industry to meet the lithium demand caused by the growing lithium-ion battery (Li-B) market. While lithium is not found in its elemental form, it can be extracted from three major sources: brine, hard-rock pegmatite, and clay deposits. In Canada, there is a significant interest in hard rock pegmatites, as they are found in several areas of the Canadian Shield [1–3]. Several lithium bearing minerals can be found in pegmatite ores, including spodumene ($\text{LiAlSi}_2\text{O}_6$), lepidolite ($\text{KLiAl}_2\text{Si}_3\text{O}_{10}(\text{OH},\text{F})_3$), petalite ($\text{LiAlSi}_4\text{O}_{10}$), and amblygonite ($(\text{Li},\text{Na})\text{AlPO}_4(\text{F},\text{OH})$) but the aluminosilicate mineral spodumene is the most commonly exploited due its relative abundance and high lithia content of about 8% Li_2O . Typical gangue minerals in pegmatite deposits include micas, feldspars, quartz, Fe-Al silicates (ex. amphiboles and other pyroxenes), and occasionally phosphate and calcium minerals [4–6]. Because of the growing battery market, most companies developing spodumene projects are targeting production of battery grade concentrates, which have specifications of $>6.0\%$ Li_2O and $<1.0\%$ Fe_2O_3 [3,7].

In general, spodumene is concentrated with a combination of dense media separation (DMS), magnetic separation, and/or froth flotation [4,6,8]. For some deposits, ore sorting can be used to reject iron at the head of the circuit at very coarse sizes, while magnetic separation can be used to reject iron at several points, like the DMS or flotation feed and/or final spodumene concentrates [4,6,8]. Spodumene concentration with DMS is achieved by rejecting gangue minerals with specific gravities (SG) lower than spodumene

(SG of 3.1–3.2). However, DMS is most effective with coarser particles (>0.85 mm), which means concentration by DMS is limited by the degree of spodumene liberation. If the grain size is too fine, it can be challenging to achieve high lithium recovery at the target concentrate grade with DMS alone. Since flotation is best suited for finer particles (<300 µm), it can be used to process a wider range of deposits, where finer grinding is required for improved spodumene liberation [4,6].

One of the biggest challenges in spodumene flotation is associated with the primary collectors—fatty acids—which are known for their strong collecting power but poor selectivity [9]. Industrial applications typically use the collector in their acid form, a nearly insoluble oily and viscous liquid, while fundamental investigations typically use the salt form, a liquid or solid with a soap-like texture that is readily soluble. The most common fatty acid appearing in spodumene flotation academic literature is oleic acid, most often used in its salt form, as sodium oleate (NaOl). Other examples of commercial spodumene collectors include tall oil fatty acids (TOFAs), synthetic fatty acids, and some oxidized petroleum derivatives like petroleum sulfonate [4,10]. TOFAs are the most common industrial spodumene collector and are mainly comprised of oleic and linoleic acids (the main components of olive oil and linseed oil, respectively), with minor rosin acid contaminants [11]. Figure 1 illustrates the primary components in TOFAs [9].

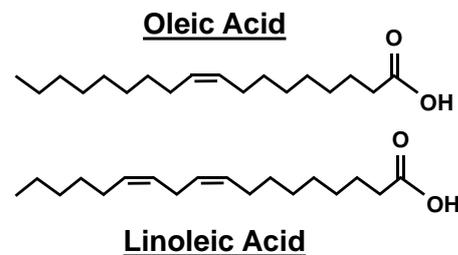


Figure 1. Molecular schematics of oleic and linoleic acid.

The poor selectivity of fatty acids is most likely related to their poor solubility, as well as their sensitivity to changes in pulp pH, collector concentration, mechanical energy input, and pulp temperature [12–14]. These changes can have a significant impact on the ionic speciation of the collectors in solution and dictate if, how, and where collector adsorption will occur on the surfaces of different minerals, suggesting that better control of collector speciation should benefit flotation selectivity [15]. The natural foaming and surfactant properties of fatty acid collectors can further hinder selectivity in flotation as they can result in the entrainment of fine gangue particles. The frothing properties of fatty acids are reported to have strong ties to their solubility, which differs with the carbon chain length, but can also be impacted by collector concentration, pH, and temperature [10,16–18]. Finally, the presence of contaminants in certain fatty acid collectors may also influence their selectivity. For example, rosin acids, the major impurities in TOFAs, have been reported to decrease selectivity by causing poor froth drainage and increasing hydraulic gangue entrainment [9,19].

Depressants (ex. polysaccharides and lignin sulfonates) have been investigated to selectively reject gangue minerals like micas, feldspars, and Fe-Al silicates, but their application can be particularly challenging in spodumene flotation as this requires the selective depression of certain silicate minerals, but not spodumene [20–23]. With specifications of <1.0% Fe₂O₃ for battery-grade spodumene concentrates and <0.17% Fe₂O₃ for ceramic or technical grade concentrates (ex. SC 7.2 > 7.2% Li₂O), improving the rejection of Fe-bearing minerals during flotation is particularly important [3,24].

In addition to spodumene, fatty acids are also used in the flotation of other minerals like metal oxides (hematite or ilmenite), salt-type minerals (calcite and phosphates), and some rare earth oxide minerals (REOs) [9,19,25–34]. As anionic collectors, fatty acids primarily interact with the surfaces of positively charged particles or cationic sites on mineral surfaces. Spodumene naturally carries a negative surface charge at the pH used

in commercial flotation (~8.5), but recovery with anionic collectors is possible due to the high concentration of cationic aluminum (Al^{3+}) sites on the spodumene surface [35]. Researchers identified that around pH 8.5, an acid–anion complex ($\text{RCOO}\cdot\text{RCOOH}^-$) was the prominent collector species adsorbed at Al sites on spodumene surfaces, which is the same species responsible for the flotation of hematite and ilmenite (adsorbed at Fe^{3+} and Ti^{4+} sites); thus, available insight into the hematite and ilmenite flotation systems may also benefit spodumene research [15,36,37].

Historically, the pegmatite deposits at King’s Mountain (North Carolina, USA) and Greenbushes (Western Australia) have provided the bulk of the world’s spodumene concentrates. Australia is currently the largest spodumene producer in the world, with production largely driven by Greenbushes along with several other smaller projects. However, there are several projects in development around the globe. Table 1 lists several operations and a few significant spodumene development projects with published head grades. Recent changes in the lithium market and projected global demand can justify the development of new spodumene projects with comparatively lower feed grades (between 0.9% Li_2O to 1.2% Li_2O) than older, historical operations (>1.5% Li_2O).

Table 1. List of several major lithium pegmatite projects including location, operating status, and lithium head grade. This list is not exhaustive.

Owner—Operation/Project	Country	Operating Status	Avg. Grade (% Li_2O)	Reference
Alliance Minerals—Bald Hill	Australia	Operating	1.00	[38]
Covalent Lithium—Mt. Holland	Australia	In Development	1.50	[38]
Talison/Albemarle—Greenbushes	Australia	Operating	2.80	[38]
Galaxy Resources—Mt. Cattlin	Australia	Operating	1.08	[38]
Mineral Resources—Mt. Marion	Australia	Operating	1.37	[38]
Pilbara Minerals—Pilgangoora Project	Australia	Operating	1.19	[39]
Albemarle/Mineral Resources—Wodgina	Australia	Operating	1.02	[38]
Sigma Lithium (Several Projects)	Brazil	In Development	1.55	[40]
Frontier Lithium—PAK	Canada	In Development	2.06	[41]
Frontier Lithium—Spark	Canada	In Development	1.37	[41]
Critical Elements—Rose Li-Ta Project	Canada	In Development	1.15	[42]
Nemaska—Whabouchi	Canada	In Development	1.55	[43]
Foremost Lithium—Snow Lake	Canada	In Development	0.91	[44]
Green Technology Metals—Seymour Project	Canada	Exploration/Dev.	1.04	[45]
Patriot Battery Metals—Corvette Property	Canada	In Development	1.30	[7]
Sayona/Piedmont—North American Lithium	Canada	In Development	1.06	[46]
Sayona Mining Ltd.—Moblan Project	Canada	In Development	1.40	[46]
Sinomine—TANCO	Canada	Operating	2.44	[47]
Jiajika Mine—Rongda Lithium	China	Operating	1.33	[48,49]
Atlantic Lithium/Piedmont—Ewoyaa	Ghana	In Development	1.26	[50]
Albemarle—Kings Mountain	USA	Recommissioning	1.50	[51,52]
Piedmont Lithium—Carolinas Project	USA	In Development	1.11	[53]

In the current market, new operations are primarily working to produce battery-grade concentrates and it is well understood that impurities within spodumene concentrates can cause issues during the downstream processing stages, increasing the overall processing costs [54]. Because of these issues, and the competition of a growing market, new operations must work to minimize impurities in their final concentrates to improve their economic value. Fatty acids have been successfully implemented as collectors to produce high-quality concentrates since the early days of spodumene flotation, but several studies today still highlight their poor selectivity and stress the need for alternatives [55–59]. One option to mitigate the selectivity issues faced by developing spodumene operations is to investigate emulsifying agents or combinations of other fatty acids to improve collector selectivity,

but it is also critical to bridge the gap between the industrial spodumene flotation process and the findings of fundamental spodumene flotation research. Commercial spodumene flotation requires NaOH scrubbing and high-density conditioning with nearly insoluble fatty acid collectors for selective flotation and high recovery. These are both aspects that are rarely discussed in fundamental studies investigating collector adsorption using soluble fatty acid salts like NaOl [12,56,57]. Because of this, it is possible that the current academic understanding of fatty acid behaviour does not fully capture the mechanisms occurring in the industrial spodumene flotation process with fatty acids.

The recovery of lithium from hard rock pegmatites has been a popular discussion topic in recent years. Several authors provide us with detailed reviews of the beneficiation and hydrometallurgy processes [4,6,60–63], but only a few reviews focus specifically on spodumene flotation [64] or flotation with fatty acid collectors [29]. This review examines the properties of fatty acid collectors in combination with their application in historical industrial spodumene flotation studies and more recent fundamental spodumene flotation research. Insight will be drawn from other fatty acid-mineral systems that rely on the same collector species for successful flotation. Our goal is to use the available fatty acid and spodumene flotation literature to provide new insight for improving their application in spodumene flotation systems to meet the needs of developing industrial spodumene projects.

2. Fatty Acid Properties

The fatty acid collectors used in spodumene flotation are carboxylic acids—organic acids containing a carboxyl group attached to an R group [65]. They are distinguished by their long hydrocarbon chains containing between 10 and 30 carbon atoms and can fall into one of two groups: saturated and unsaturated, where unsaturated chains come from the presence of one or more double bonds between carbon atoms in the molecule (Figure 1) [9,65]. Unsaturated fatty acids are most prevalent in flotation collectors. While purified versions of these compounds can be made synthetically, they are also found naturally in plants (ex. trees), animals, and vegetables, with the exact composition depending on the source [10,66]. For example, TOFAs—a byproduct of the paper making process—contain impurities like rosin acids which remain in minor amounts after the purification process. Table 2 presents a summary of common fatty acids and rosin acids and their chemical formula.

Table 2. Different types of fatty and rosin acids with their respective chemical formulas [9]. * Different rosin acids have the same chemical formula, but their structures differ (i.e., isomers).

Acid Type	Chemical Name	Chemical Formula
Saturated	Lauric Acid	$\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$
	Palmitic Acid	$\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$
	Stearic Acid	$\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$
Unsaturated	Oleic Acid	$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$
	Linoleic Acid	$\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$
	Linolenic Acid	$\text{CH}_3(\text{CH}_2)_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$
Rosin	Abietic Acid	$\text{C}_{20}\text{H}_{30}\text{O}_2$
	Palustric Acid *	$\text{C}_{20}\text{H}_{30}\text{O}_2$
	Neoabietic Acid *	$\text{C}_{20}\text{H}_{30}\text{O}_2$

Oleic acid is the most common fatty acid cited in industrial spodumene flotation research (i.e., bench-scale flotation on real ores), while fundamental studies often use the more soluble NaOl ($\text{C}_{18}\text{H}_{33}\text{NaO}_2$). Commercial operations tend to use TOFAs (containing oleic, linoleic, and minor amounts of rosin acids) as a more cost-effective option. Commercial TOFA producers, like Kraton Corporation, offer several products with varying rosin contents. Their two primary fatty acid products sold to the mining industry are Sylfat FA1 containing approximately 3% rosin acids, and Sylfat FA2 containing approximately 1%

rosin acids. FA2 was used in the flowsheet development work for both Critical Elements' Rose Lithium-Tantalum Project and Nemaska Lithium's Whabouchi Project [11,42,43].

The preferred use of NaOH in fundamental research is likely due to its improved solubility, while theoretically exhibiting identical properties to oleic acid. In commercial spodumene operations, high density conditioning (~60% solids w/w) is required to successfully incorporate fatty acids into the pulp; replicating this process can be difficult in small-scale fundamental investigations. The high pulp density provides a mechanical mixing component that likely improves dispersion of the insoluble collector during the conditioning stage. In some applications (although not in spodumene flotation), TOFAs are subjected to a saponification process at high pH to produce carboxylate salts (like NaOH), increasing collector solubility [10]. Interestingly, there is little discussion in literature about how and why flotation performance changes when collectors are added as pure fatty acids compared to their salt form. Several studies indicate factors like solubility, speciation, and species concentration impact the collection and frothing behaviour of fatty acids during flotation, which suggests that a more critical understanding of flotation performance with pure fatty acids versus their salt forms is needed [14,18,29,35,67–70]. This section reviews the fundamental properties of fatty acid collectors and similar shorter chain carboxylic acids to aid in understanding their role in selective spodumene flotation.

2.1. Distribution of Species in Solution

Long chain unsaturated fatty acids ($\text{RCOOH}_{(l)}$) are typically liquid at room temperature and are nearly insoluble soluble in water, particularly at low pH [14,71]. As shown in Figure 2, there is a very low concentration of the soluble portion ($\text{RCOOH}_{(aq)}$), which will reversibly dissociate in solution to form an H^+ atom and a carboxylate anion (RCOO^-). The dissociation constant (K_a) is a ratio of the concentration of products divided by that of reactants in the dissociation reaction. The pH at which the concentration of $\text{RCOOH}_{(aq)}$ and RCOO^- in solution are equal is referred to as the pK_a ; higher pK_a values indicate weaker acids like TOFAs [72]. The forms of fatty acids present in solution at a constant total concentration are best represented through a species distribution diagram. The species distribution diagram in Figure 2 is adapted from the work of Pugh and Stenius [14] and shows the calculated concentrations of different species in solution for oleic acid across different pH values at a constant total concentration of 3.0×10^{-4} M.

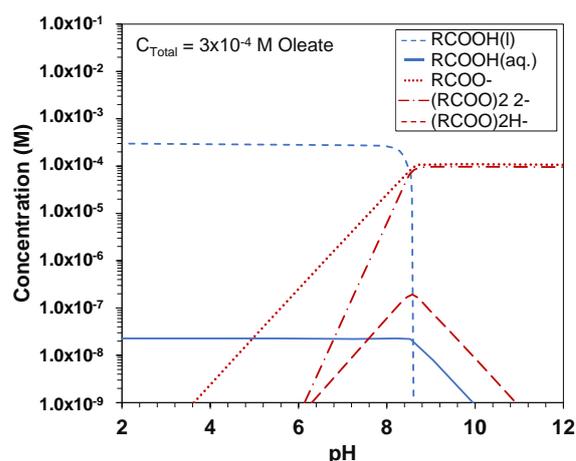


Figure 2. Species distribution diagram for 3.0×10^{-4} M oleic acid, adapted from [14].

The plot in Figure 2 indicates the presence of three ionic species in solution at higher pH values: the oleate carboxylate anion (RCOO^-), the oleate dimer ($[\text{RCOO}]_2^{2-}$), and the acid–anion complex ($\text{RCOO} \cdot \text{RCOOH}^-$); the formation of which occur at pH 3.6, pH 6, and around pH 6.2, respectively. The equilibrium constants used in the oleate calculations were adopted from earlier work of Ananthapadmanabhan et al. [73], who conducted similar studies with oleate and amines. In this work, the pK_a for oleate (C_{18}) was obtained

by extrapolating the pK_a values of shorter chain carboxylic acids and the dimerization constants were estimated by assuming a linear relationship between the logarithm of solubility and chain length. The authors also discussed the formation of an acid–anion salt ($[\text{RCOO}]_2\text{HNa}$) at total concentrations above the precipitation limit and an acid dimer ($[\text{RCOOH}]_2$), but the dimer was omitted from calculations due to the lack of available equilibrium data. When the concentration is relatively low, the formation of the acid–anion complex is considered more thermodynamically favorable than oleate dimers, which may explain its role in spodumene flotation [14,74]. Compared to shorter chain fatty acids, long chain unsaturated fatty acids have notably more ionic activity due to the formation of complexes and dimers which provide stronger collector–particle interaction with the spodumene surface.

As shown in Figure 2, high concentrations of all species ($\text{RCOOH}_{(\text{aq})}$, $\text{RCOOH}_{(\text{l})}$, RCOO^- , and $(\text{RCOO})_2^{2-}$) appear around pH 8.6 where the concentration of acid–anion complex is at its peak. Pugh and Stenius [14] confirmed this through surface tension measurements of a 3.0×10^{-4} M NaOl solution at different pH values. Below pH 8, the surface tension was around 38 mN/m. As pH increased above 8, the surface tension decreased to a minimum of 29 mN/m, until increasing again after pH 9.5 and plateauing at 35 mN/m above pH 11. The minimum surface tension confirmed the increased ionic activity and the authors theorized that the minimum surface tension is tied to the presence of the acid–anion complex, highlighting that the surface tension was highest in pH regions where this species should not form. At different total concentrations, the authors also reported shifts in the pH maximum concentration for the acid–anion complex—higher pH at lower total concentrations and lower pH at higher total concentrations [14].

It is clear from Pugh and Stenius [14] that the total collector concentration impacts speciation and can impact collector speciation. Dosages in flotation are typically noted on a grams per tonne (g/t) basis, often with little attention given to molar concentrations in solution. However, based on the speciation behaviour of fatty acids, it can be argued that more attention should be given to total concentration in solution to ensure proper conditioning in fatty acid flotation.

2.2. The pK_a Value

pK_a values are used to develop species distribution diagrams, like that presented in Figure 2. Generally, the pK_a indicates an acid's strength; as the pK_a increases, acidic strength decreases along with the ability of the acid to give up a proton (H^+). However, there is some debate over the exact pK_a values of fatty acids, with contradicting values appearing in the literature. The two methods discussed for determination of the pK_a are electrophoretic mobility and acid–base titration which report different findings as chain length increases and solubility decreases. The results with both techniques agree that shorter chain saturated carboxylic acids, up to C_8 , have pK_a values around 4.8. However, for a C_{18} saturated fatty acid, the reported pK_a varied from pH 4.7 when measured with electrophoretic mobility, to nearly pH 10 when measured with acid–base titration [30,75]. This is noteworthy because using a pK_a of 10 to design the oleic acid species distribution diagram significantly impacts our current understanding of fatty acid behaviour and spodumene flotation.

Smith [76] stated that the pK_a for fatty acid collectors of differing chain lengths such as capric (C_{10}), lauric (C_{12}), palmitic (C_{16}), oleic (C_{18}), and linoleic (C_{18}) acids were all around $\text{pH } 4.7 \pm 0.5$, and that pK_a values can be estimated by comparing the structure with that of other similar organic compounds—assuming they have similar dissociative behaviour. Like Smith, other publications, mainly using electrophoretic mobility, presented pK_a values of long chain fatty acids to be 4.7, 4.8, 4.9, 5.1, and up to 5.3 [14,26,30,69,73,77].

The use of electrophoretic measurements to determine the pK_a of fatty acids was described by Growney and Lewis [78]. The authors plotted mobility measurements against pH and used the resulting curves to determine the pK_a . It was assumed that dissociation of $\text{RCOOH}_{(\text{aq})}$ into RCOO^- occurs along the linearly decreasing section of a curve like that shown in Figure 3. With this assumption, the mobility at the minimum plateau

was presumed to be the point of complete dissociation. This value was then halved to determine the half dissociation point, the pH of which should equal the pK_a . The authors of the original data used in Figure 3, Mehrishi and Seaman [79], observed that the linear behaviour of the curve indicates the presence of only one acidic group, meaning this is the region where dissociation occurs.

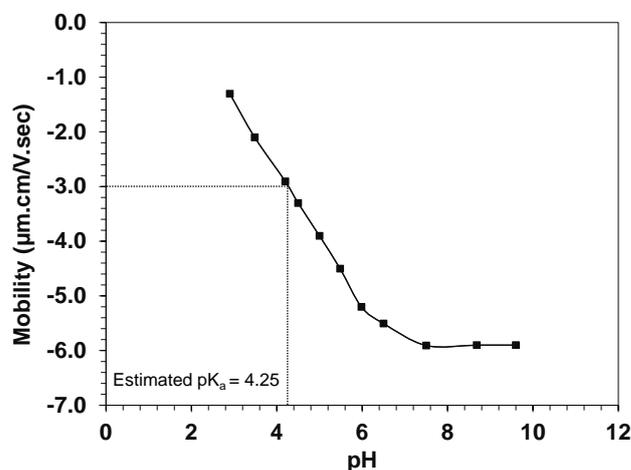


Figure 3. Determination of pK_a from electrophoretic mobility measurements for stearic acid, adapted from [79].

The method of electrophoretic mobility was repeated with stearic acid by Usui and Healy [80]. Results indicated the pK_a of stearic acid was around pH 4.5 and pH 4 at concentrations of 10^{-4} M and 10^{-2} M, respectively. These values compare reasonably well with values calculated based on the principles in colloid chemistry, which were pH 5.3 and 4.8, where the lower pK_a values correspond to a higher acid concentration. Quast [30] published a study investigating the use of zeta potential measurements of electrophoretic mobility to determine the pK_a values for C_{10} to C_{18} saturated fatty acids. The study found an average pK_a value of 4.01 with a standard deviation of 0.32 for all the fatty acids tested, indicating little variation with chain length.

Quast often references work published by Kanicky and Shah [75] who used acid-base titration to determine the pK_a for different fatty acids up to C_{18} and reported pK_a values up to pH 10 (Figure 4). Quast comments that the concentrations tested were above the critical micelle concentration (CMC) and resulted in the presence of micelles in the bulk solution which may have affected the reported pK_a values. A closer look shows that Kanicky et al. [16] conducted experiments below the CMC in initial work, with up to C_{16} fatty acids, but above the CMC in subsequent work with different C_{18} acids [75,81]. The main issue with testing above the CMC is that the introduction of micelles into the bulk solution which will likely skew the pK_a measurement with electrophoretic mobility, but the impact of micelles on titration results is less clear. Aside from micelles, Kanicky and Shah (2002) stated that small aggregates such as dimers, trimers, and tetramers may be present in C_{18} acid solutions, as well as undissolved fatty acid precipitates. It is possible that the presence of these aggregates and precipitates impacted the pK_a measurement with acid-base titration. Unfortunately, oleic and linoleic acids, the common components of TOFA, were only tested above the CMC and it is uncertain how results would differ at lower concentrations [30,75,81].

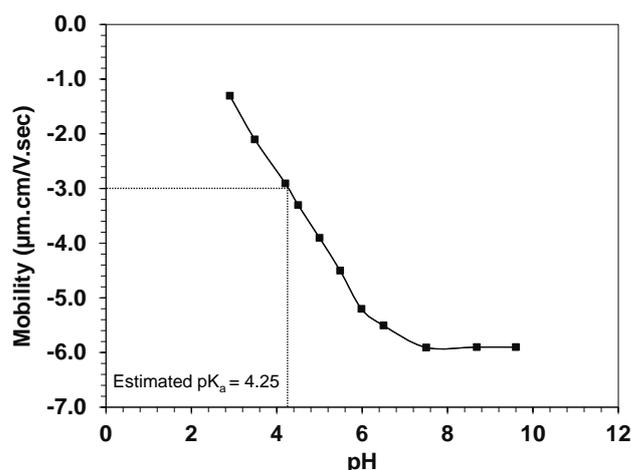


Figure 4. Measured pK_a versus carbon chain length for different carboxylic acids using the titration method, adapted from [75].

Kanicky et al. [16] performed titrations with C_6 to C_{18} carboxylic acids dissolved in a pH 10, 0.1 M NaOH solution to determine their pK_a . Dilute HCl was slowly added to lower pH, and the neutralization point was determined from the inflection on a traditional “S” shaped titration curve. The pK_a was calculated to be the pH on the curve at which 50% of the volume needed to reach neutralization had been added. The data presented in Figure 4 reflect an unexpected increase in pK_a at carbon chain lengths greater than 6, from about 4.7 to about 8.1 for a chain length of 14. When tested above the CMC with C_{16} and C_{18} acids, the trend of increasing pK_a vs. chain length is maintained, which suggests that the titration measurements may not have been impacted by exceeding the CMC.

The authors report that this increase in pK_a was caused by increased van der Waals and polar group interactions with longer chain fatty acids. For longer chain acids, it was proposed that an increase in these interactions reduced the intermolecular distance within solution and made it more difficult for the acid to donate a proton, which resulted in an increased pK_a [16,75,81]. The same principle of pK_a determination has been used by other authors, who have reported similar values for longer chain saturated and unsaturated acids up to C_{18} [82,83]. More recently, Wellen et al. [84] used surface tension titration at the air–water interface to determine the pK_a of C_6 , C_8 , and C_{10} chain carboxylic acids and reported values of 4.9, 5.8, and 6.4, respectively, in agreement with Kanicky and Shah.

There is clear debate over the pK_a of fatty acids in the existing literature, particularly for longer chain acids like oleic and linoleic acid. Using distribution diagrams based on the electrophoretic mobility pK_a measurements, spodumene research has determined that the fatty acid species adsorbing onto the particle surfaces is the acid–anion complex, which occurs in the neutral to slightly alkaline region of Figure 2. If these diagrams are incorrect, it could impact the current understanding of the oleic acid flotation systems. However, it is important to highlight that the current understanding of spodumene flotation aligns well with pK_a values reported with electrophoretic mobility, as the maximum concentration of acid–anion complex is around pH 8.5, which corresponds to the typical pH in used to float spodumene [8,35,37].

2.3. Frothing Properties

Controlling the froth in flotation is critical to selective mineral recovery and fatty acids are notorious for their froth challenges. Poor froth properties (ex. structure, stability, and thickness) can lead to hydraulic entrainment of fine gangue and froth drainage issues that reduce concentrate quality and flotation performance. Frothers such as polyglycols or methyl isobutyl carbinol (MIBC) are typically required in flotation to generate fine bubbles and improve froth stability in systems where separate collectors and frothers are required. However, fatty acids have a dual function and can provide both the frothing and collecting

power in flotation systems like spodumene. A strong understanding of the fatty acid frothing behaviour under different conditions is needed to optimize spodumene flotation circuits [9,56,85].

Kanicky et al. [16] evaluated the foaming properties of a C_{16} fatty acid by vigorously shaking a 20 mL sample in a 100 mL graduated cylinder for 30 s and observed the pH of the maximum foam height increased with increased chain length, like that of the pK_a . More recently, Atrafi et al. [18] analyzed the frothing properties of NaOl, TOFA, and MIBC solutions by measuring gas dispersion and foaming properties. Results showed NaOl and TOFA produced a larger bubble size and had weaker frothing power than MIBC—a relatively weak frother. Figure 5 shows the relationship between concentration, bubble size, and foamability for NaOl, TOFA, and MIBC. The plateau of the MIBC curve at a bubble size of around 1 mm is referred to as critical coalescence concentration (CCC); above this concentration there will be little decrease in bubble size. At natural pH, the CCC of both TOFA and NaOl was about 70 mg/L, while for NaOl at pH 10, the CCC was reduced to about 50 mg/L. The lower CCC at higher pH is likely the result of the increased solubility of fatty acids in this pH range, suggesting that frothing properties are connected to the speciation behaviour. The nature of the TOFA curve in relation to that of NaOl was not discussed in this study, the major difference being that TOFA also contains linoleic acid and other impurities like rosin acids which may have slightly increased the minimum bubble size. Figure 5 indicates that the bubble size at the CCC of MIBC, NaOl, and TOFA was similar, between 1.0 mm and 1.6 mm, but the required concentration to achieve this bubble size with NaOl and TOFA was significantly higher than that of MIBC.

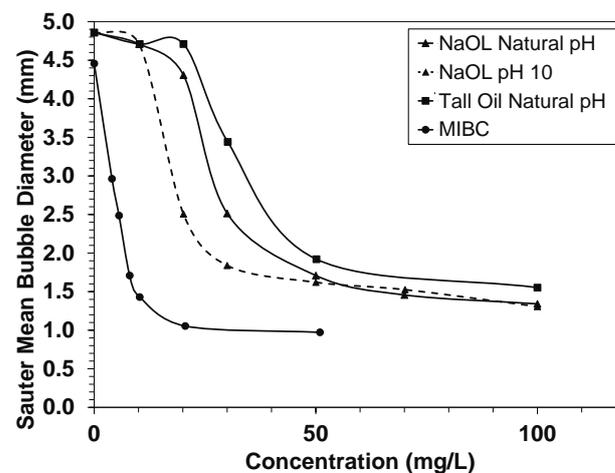


Figure 5. Solution concentration vs. mean bubble diameter for TOFA, NaOl, and MIBC, adapted from [18].

One major observation made by Atrafi et al. [18] is the tendency of the froth layer in fatty acid solutions to grow continuously until catastrophic failure, never reaching steady state conditions. While the reason for this is uncertain, it could be tied to depletion of fatty acid in solution as froth height increases. With a typical frother (ex. MIBC or a polyglycol), it is common to observe simultaneous collapse and growth of froth, resulting in a stable froth layer. In the NaOl system, there was little to no foam observed at concentrations below 30 mg/L, but above this concentration there was a dramatic increase in foam height that continued as concentration increased to 50 mg/L. Above 50 mg/L, the maximum foam height plateaued and, regardless of concentration, all tests exhibited a final catastrophic failure, meaning the froth layer quickly decreased until it no longer existed.

The author also considered the impact of pH on the frothing properties of NaOl at two different concentrations: 20 mg/L (natural pH of 7) and 70 mg/L (natural pH of 8.4). Figure 6 presents the foamability behaviour of the two NaOl solutions between pH 5 and 10 at an air rate of $400 \text{ cm}^3/\text{min}$; measurements were reported until froth failure. Results

showed the foamability of NaOl was heavily dependent on both pH and total concentration. At $\text{pH} < 7$ for 20 mg/L and $\text{pH} < 5.9$ for 70 mg/L, little to no foam was observed, but both solutions exhibited foaming at pH values above these points. The total gas volume in solution reached a maximum at around pH 8 but decreased slightly as pH further increased to 10. The pH of maximum foamability of these solutions at their respective concentrations corresponds well with the pH of minimum surface tension reported by Pugh and Stenius [14]. The disappearance of the insoluble acid phase and formation of the oleate anion also occurs at this pH, as does the maximum concentration of the acid–anion complex.

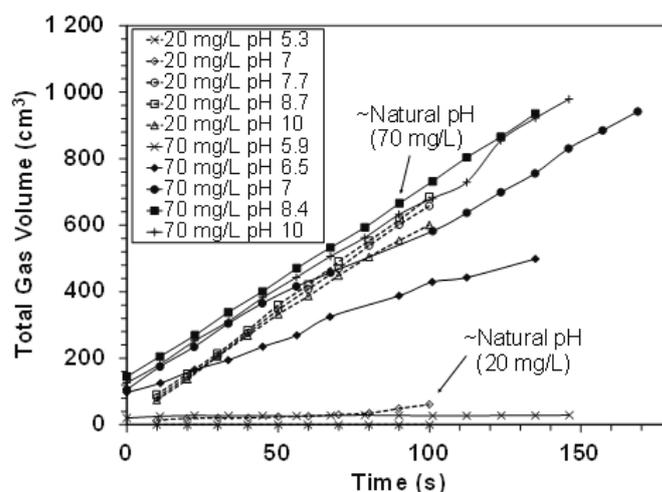


Figure 6. Total gas volume versus time for 20 mg/L and 70 mg/L solutions of NaOl between pH 5 and 10, adapted from [69].

Thus, similar maximum foam heights were reported by Kanicky et al. [16] and by Atrafi [69]. Both studies suggested that the soluble anionic species contributed to the froth height and stability, as they are not present in significant concentrations at lower pH; and that the insoluble acid may be harmful to froth properties. To confirm the negative impact of insoluble acid on froth properties, Atrafi [69] combined a high dose of MIBC to minimize the CCC in a NaOl solution at low pH to ensure a high amount of insoluble acid. The findings demonstrated that the presence of insoluble acid cut the foamability of MIBC in half. The author also observed that the insoluble liquid acid was carried out in the froth layer, concluding that its presence in the froth layer was likely responsible for the decreased foamability.

The work of Atrafi provides good insight into the frothing behaviour of fatty acid collectors by indicating the limits of pH and concentration where high foamability occurs. It also agrees with the observations of previous researchers and may provide some explanation as to why frothers like MIBC are rarely used in spodumene flotation. The author's investigation with TOFA was limited to natural pH, so it is difficult to say how pH and concentration limits for foaming behaviour would differ from NaOl because of other components like linoleic and rosin acids. Regardless, there is a clear overlap between the operating regions of pH and fatty acid concentration needed for good spodumene recovery and the regions of high foamability. An expansion of this work with TOFA could better describe the effect of the pH and concentration (mg/L or M) on frothing properties and help to pinpoint the conditions needed to optimize froth properties in commercial spodumene flotation systems.

2.4. Solubility

Poor solubility is a major obstacle in spodumene flotation with fatty acid collectors. Understanding the solubility behaviour is important in selecting collector dosage, as flotation must occur in the range where both the anionic and molecular acid forms exist.

This is influenced by several factors including pulp pH, pulp temperature, and collector dosage (concentration). For example, flotation operations located in cold climate regions, such as Canada, may condition the pulp at lower temperatures which could result in solidification of the fatty acid collectors and simultaneously decrease their solubility. While solubility of carboxylic acids is high at low chain lengths, like acetic acid (C₂), it decreases significantly as chain length increases.

There are frequently cited data available on the solubility limits of different saturated fatty acids at increased temperature, but the same information for mono and polyunsaturated fatty acids is difficult to find. The Merck Index (an encyclopedia of chemicals, drugs, and biological substances) states that NaOl is soluble up to 100 mg/mL in solution, but it is unclear if heat is needed or how pH impacts solubility [86]. This likely explains why NaOl is used over oleic or linoleic acid in small-scale fundamental flotation investigations since the latter are reported to be practically insoluble [71]. While it is common for certain TOFA flotation applications to perform conditioning at elevated temperatures to enhance solubility, poor solubility in spodumene flotation is typically overcome using high pulp density during conditioning rather than high temperature. High pulp density helps to enhance collector dispersion into the slurry (like emulsification), while potentially improving collector solubility at the same time [87]. Complete fatty acid solubility is not ideal, as the concentration of the molecular acid, needed for spodumene flotation, would be very low.

Solubility is thought to be higher in unsaturated fatty acids with a higher number of double bonds as these double bonds have polar characteristics that can attract water molecules [88,89]. Another technique to improve solubility is increased temperature. The impact of temperature on fatty acid solubility was studied by Ralston and Hoerr [88] between 0 °C and 60 °C, and later by Eggenberger et al. [90] at between 30 °C and 60 °C. Each study reported slightly different results but with the same general trends. Ralston and Hoerr state that all carboxylic acids, C₆ to C₁₈, are soluble at temperatures from 0 °C to 60 °C, with very low solubilities for longer chain acids at room temperature and below. Eggenberger et al. only tested C₈ to C₁₄ carboxylic acids and reported the C₁₂ and C₁₄ fatty acids were both insoluble at 30 °C and lower, but became soluble at 40 °C and 50 °C, respectively. There was no discussion of solution pH in either study, thus it may be assumed they were operating at natural pH.

As reported by Atrafi [69], too much insoluble acid is detrimental to the frothing behaviour of fatty acids, so an understanding of collector solubility is important. However, the best fatty acid flotation performance of minerals like spodumene occurs in the slightly alkaline region between 7 and 9, where both insoluble acid and anionic species are present. The dual frothing and collecting properties of fatty acids are required for successful flotation but the optimization of these properties remains challenging. The most common pK_a values, determined through electrophoretic mobility measurements, helped determine the species distribution diagrams used to explain spodumene flotation. Because of sensitivity to pulp conditions, a strong understanding of how pH, temperature, concentration, and mechanical components (like high-density conditioning) impact solubility and collector speciation is essential for improving the application of fatty acids in spodumene flotation.

3. Fatty Acids in Spodumene Flotation

As discussed, long chain saturated fatty acids are the most common collectors in spodumene flotation because of their chemical affinity for the spodumene surface, but selective recovery can be a major obstacle. Several industrial publications from 1930s to the 1990s discuss the progression of spodumene flotation with fatty acids from North American, Canadian, and Australian pegmatite ores. These publications highlight how spodumene can be successfully floated with fatty acids to produce high grade concentrates and high lithium recoveries, while also discussing the various challenges to achieve this performance at an industrial scale [8,13,20,21,39,56,57,91–94]. Unfortunately, fundamental explanations of spodumene flotation were rare until the 21st century.

Research over the past 20 years has heavily focused on fundamental research and provides good insight into the mechanisms of spodumene flotation. While there are inconsistencies in spodumene recoveries reported across different fundamental studies that used nearly identical procedures, there is general agreement that the adsorption of fatty acids onto spodumene relies on the chemical reaction between an anionic fatty acid (carboxylate) species and the cationic Al^{3+} sites on spodumene surfaces—the acid–anion complex [35–37,95]. A large portion of work from the last 5 years out of China has heavily focused on collector design to improve spodumene recovery and selective rejection of feldspar. Much of this work investigated the combined use of cationic amine collectors and NaOl, or the potential benefit of cationic activators such as Ca^{2+} , Mg^{2+} , or Fe^{3+} in the spodumene-oleate system [95–106].

The fundamental study of commercial fatty acid collectors, like TOFA, in spodumene flotation remains limited, likely due to their poor solubility which poses practical challenges when used at small-scale. Once again, the bulk of the academic research discusses NaOl as the primary fatty acid collector—as a proxy for oleic acid—because it is readily soluble and spodumene flotation performance with NaOl and oleic acid is assumed to be identical. However, there are some discrepancies between fundamental spodumene flotation results using pure NaOl and results of spodumene flotation from real ores using oleic acid. This suggests the differences in the speciation behaviour of these two collectors requires a better understanding and that fundamental studies using NaOl may overlook some aspects required for successful flotation of spodumene with commercial fatty acid collectors from real pegmatite ores.

3.1. Fundamentals of the Spodumene-Oleate Flotation System

The basics of spodumene flotation are important to understand before discussing the findings of historical and more recent industrial studies with real ore systems. Most fundamental research into spodumene flotation uses single mineral systems to isolate collector-particle interactions. In 2003, Moon and Fuerstenau [35] conducted one of the first comprehensive studies evaluating the oleate adsorption mechanism and spodumene surface crystal chemistry through single mineral microflotation, adsorption measurements, Fourier Transform Infrared spectroscopy (FTIR), contact angle measurements, and zeta potential measurements. The zeta potential measurements and microflotation results are presented in Figure 7a and Figure 7b, respectively. Spodumene recovery reached a maximum of ~100% around pH 8 at NaOl concentrations of 10^{-4} and 10^{-3} M, corresponding to a distinct minimum in zeta potential; the maximum oleate adsorption onto spodumene surfaces was also reported at pH 8.

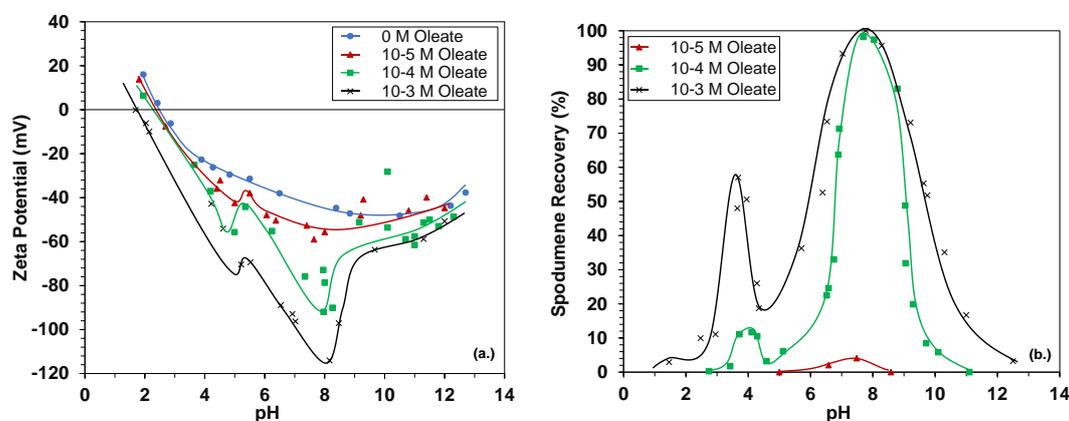


Figure 7. Zeta potential (a) and spodumene recovery (b) vs. pH for different NaOl concentrations, adapted from [35].

Using a polyhedral model of the spodumene crystal structure to evaluate the cleavage surfaces at an atomic level, the authors reported that the two weakest (most common) cleavage planes in the spodumene crystal, [110] and [001], have different concentrations and configurations of Al sites because of differential breakage of Al-O bonds. The [110] plane has a higher concentration of Al³⁺ sites and two broken Al-O bonds, giving it a higher affinity for oleate. The affinity for oleate adsorption around pH 8 increased after pretreatment with NaOH, which increased the number of Al³⁺ surface sites by further breaking Al-O bonds. This treatment is comparable to NaOH scrubbing, or activation, typically used in industrial spodumene flotation (often described as a means to combat ‘surface weathering’) to enhance collector adsorption [8,55]. The increased oleate interaction after the NaOH treatment was confirmed through contact angle measurements, which were significantly higher on the [110] plane; increased oleate interaction with the [110] cleavage plane was also confirmed by other studies [58,95,106,107]. A small peak in recovery was also observed around pH 4 (10⁻³ M NaOH), which Moon and Fuerstenau attributed to the interaction of oleate with iron impurities within the spodumene crystal structure.

A similar relationship between surface site concentration and flotation performance—and possibly collector dosage—has been discussed in other fatty acid flotation systems like hematite and ilmenite. Mehdilo et al. [15] observed a strong relationship between the concentration of available Ti⁴⁺ and Fe³⁺ sites on the ilmenite surface and flotation recovery, with higher recoveries possible when more adsorption sites are available. It is unclear if higher collector dosages could improve recovery as this was not investigated. However, the fatty acid dosages used to float hematite—which has a high concentration of Fe³⁺ sites—are significantly lower than those used in spodumene or ilmenite research (10⁻⁵ M vs. 10⁻⁴ M NaOH, respectively) and suggests that a relationship between available adsorption sites and fatty acid dosage exists [36,108].

Xu et al. [58] and Tian et al. [106] discussed the impact of particle size on the concentration of [110] planes and its impact in spodumene flotation. The authors performed single mineral microflotation tests on +53/−75 μm, +38/−53 μm, +19/−38 μm, and −19 μm spodumene samples. A peak in spodumene recovery occurred at pH 8.5 for all size fractions, but without NaOH pretreatment, the highest reported recovery was ~40% with the +38/−45 μm size fraction. Spodumene recovery was lowest in the −19 μm size fraction, at around 18%. There was no mention of NaOH treatment to improve collector adsorption and instead, the authors introduced Fe³⁺ as an activator which improved recovery in these two size fractions to about 90% and 70%, respectively, with the maxima still occurring at pH 8.5. The lower recovery in the finer fraction was attributed to reduced concentration of [110] planes and increased concentration of [001] planes on the spodumene surface at small particle sizes. This response agrees with the lower contact angles on [001] planes reported by Moon and Fuerstenau [35]. The desliming of particles < 15–20 μm is standard practice in the flotation of real spodumene ores as gangue particles in this size range are prone to hydraulic entrainment [8,55,107]. It is also possible the higher particle surface area in the finer size fractions played a role in the lower spodumene recovery as particles in this size range may require a higher collector dosage to improve recovery.

Yu et al. [37] investigated the mechanism of oleate adsorption onto the spodumene surface using microflotation and Density Functional Theory (DFT) in one of the few fundamental spodumene studies to use oleic acid instead of NaOH. This study reported maximum spodumene recoveries between 75% and 80% using 6.0 × 10⁻⁴ M oleic acid at pH values between 8 and 9; outside this pH range recovery quickly fell below 50%. DFT results determined complexes of acid molecules and oleate anions held together by Van der Waals forces (acid–anion complexes) were responsible for the improved flotation behaviour at this pH. This was supported by species distribution diagrams of oleic acid at 6.0 × 10⁻⁴ M which indicated the concentration of acid–anion complex in solution reached a maximum around pH 8.7. These values coincided well with the regions of maximum foamability reported by Atrafi [69] and further support the theory that both the oleate anion and molecular oleic acid species are needed for successful flotation. However, the authors

did not discuss the formation of this complex. It is unclear if the acid–anion complexes were present in solution, as suggested by the distribution diagram in Figure 2, or if the mechanical input from conditioning promoted their formation either in solution or on the spodumene surface.

Fundamental studies of the pure oleate–spodumene system provide insight into adsorption mechanisms of fatty acids at the spodumene surface. While there is agreement that chemisorption of an anionic oleate species at the Al^{3+} surface sites renders spodumene hydrophobic, it was Yu et al. [37] that first stated the chemisorbed species was an acid–anion complex, something that has been discussed in other mineral systems (ex. Hematite and ilmenite) as early as 1980 [108]. Only Moon and Fuerstenau [35] used NaOH to activate the spodumene surface (as is practiced commercially), and thus it is possible the need for Fe^{3+} activators in the work of Xu et al. [58] and Tian et al. [106] may have been mitigated had the authors first treated the particles with NaOH. The varying recoveries reported in small-scale flotation studies with oleate suggest that more consistency is needed in fundamental spodumene studies and that researchers may benefit from leveraging phenomena observed in real ore flotation systems to small scale flotation research.

3.2. Investigations with Real Spodumene Ores

3.2.1. Historical Research (before 2000)

The work of Moon and Fuerstenau [35] was based on phenomena first observed in the flotation of real spodumene ores. From the mid-20th century until the 1990s, the United States dominated global spodumene production from operations near King’s Mountain, North Carolina owned by the Foote Mineral Co. and Lithium Corp. of America. With head grades averaging around 1.5% Li_2O and significant reserves, this region produced spodumene concentrate for nearly 50 years. In response to today’s growing lithium demand, new and old spodumene projects are again being developed in the region [8,51,53]. The 50 years of spodumene concentration test work using ore from the King’s Mountain region and other smaller deposits across the United States provided the basis for early fundamental studies and offers insight into why fatty acids are still the primary collectors used today.

Initial Flowsheet Development and Collector Testing

As early as 1940, Norman and Gieseke [55] outlined a process (very close to that reported in many development projects today) to concentrate spodumene from King’s Mountain ore by flotation with fatty acid collectors. A similar process was later adopted by Solvay Process Co. from 1943 to 1946 at the initial King’s Mountain spodumene operation. Preliminary testing on a ‘low-grade’ ore (2.5% Li_2O with high weathering) and a ‘high-grade’ ore (containing up to 4.0% Li_2O) resulted in successful spodumene flotation with oleic acid-based collectors, which performed best in slightly alkaline conditions. One rougher and two cleaner flotation stages were performed to upgrade the weathered ore, and just one cleaner was required to upgrade the high-grade ore. Norman and Gieseke also successfully upgraded spodumene by flotation from several other ores across the United States (Lincoln, N.C.; Dixon, N.M.; Warren, M.E.; Tinton, S.D.) following a similar process to that used at Kings Mountain, with oleic acid dosages between 400–750 g/t.

In 1946, Munson and Erickson [91] successfully applied a similar method of fatty acid spodumene flotation to upgrade material from the Edison Mine in Keystone, South Dakota. In this study, the authors evaluated different water sources to use during operation and determined that high concentrations of Ca^{2+} and Mg^{2+} had an adverse impact on spodumene flotation performance and potentially interacted with the fatty acid collector. Later testing by Munson and Clarke in the 1950s determined the general flowsheet developed by Norman and Gieseke could be used to concentrate spodumene from other spodumene deposits from the Black Hills of South Dakota [109].

In addition to fatty acids, Norman and Gieseke investigated spodumene flotation with naphthenic acids, naphthenic soaps, sulphonated castor oil, phosphorated castor oil, ammonium sulphoricinoleate, which worked best under acidic conditions, but all

were inferior to fatty acids [55]. Later, Bhappu and Fuerstenau [110] and Purcell and Bhappu [111] successfully floated spodumene with sulfonate collectors between pH 2.5 and 4.5. While less popular for commercial spodumene flotation, sulfonates were used as collectors to float Fe-silicate gangue from the spodumene tailings during by-product flotation for feldspar and quartz [56,57]. In the 1960s, another cheaper alternative anionic collector was proven by Weir and Moskovits [92] who successfully concentrated spodumene from a Mt. Marion, Western Australia ore using an emulsion of sulphonated whale oil, linseed fatty acids, cresylic acid, and diesel fuel oil around pH 8.2; however, the use of this collector was never applied in commercial operation.

Pre-Treatment with NaOH

Initially, selective separation with fatty acid collectors was only possible with higher-grade ores but after several experiments, Norman and Gieseke [55] identified that lithium recovery from lower-grade, weathered ore could be improved by scrubbing with sodium hydroxide (NaOH) at about 50% solids for 20–30 min. Other scrubbing reagents such as sodium silicofluoride (Na_2SiF_6), trisodium phosphate (Na_3PO_4), and sodium sulphide (NaS) were investigated, but NaOH provided the best results with optimal scrubbing time and dosage directly related to the extent of surface weathering. After scrubbing, the ore was deslimed to remove fine particles ($<20\ \mu\text{m}$) from the feed, which accounted for about 10% of the feed mass. The pulp was then washed free of NaOH before conditioning with the fatty acid collector.

Conditioning with Fatty Acids

In 1961, Browning and McVay [13] investigated fatty acid conditioning through batch flotation testing of King's Mountain ore using 750 g/t oleic acid. The authors evaluated the impact of (1) conditioning and flotation pH using different pH modifiers (Figure 8a), and (2) conditioning pulp density (Figure 8b) on spodumene flotation performance. The best flotation results were reported when conditioned at pH 6.8, producing a concentrate grade of 6.7% Li_2O with 84% lithium recovery. Flotation performance suffered as pH increased, more so when soda ash was used as a pH modifier compared with NaOH. Although it was not discussed in Browning and McVay's research, we now know that decreased recovery corresponds to decreased concentration of the acid–anion complex at higher pH values. Further, reduced performance with soda ash was a clear indication that the chemical species in soda ash were detrimental to conditioning performance. Further research is required to understand the impact of soda ash during fatty acid conditioning at a fundamental level.

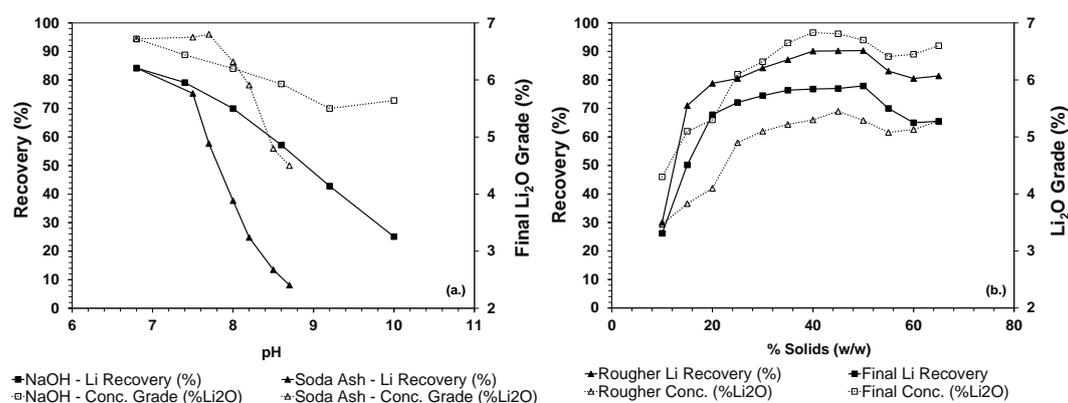


Figure 8. Impact of pH Modifier (a) and percent solids (b) on spodumene flotation performance, adapted from [13].

The effect of pulp density was investigated between 10% and 65% solids w/w with the best performance achieved between 40% and 50% solids, producing a concentrate grade of 6.8% Li_2O with 77% lithium recovery. At lower pulp density, the grade and recovery

both decreased, with concentrate grade dropping quickly at densities below 25% solids. As the pulp density increased (50–65% solids), the recovery dropped but the final concentrate grade was maintained [14]. Ultimately, the study clearly identified a connection between pulp density in fatty acid conditioning and spodumene flotation performance but failed to clearly explain how percent solids impacted spodumene flotation performance. However, we know that changing percent solids while keeping collector dosage (g/t) constant changes the collector concentration (mg/L) as the ratio of solids to water changes. Any change in collector concentration, particularly a reduction caused by lower percent solids, will influence the collector speciation, and reduce spodumene recovery, as shown by Moon and Fuerstenau [35]. Another potential factor is the mechanical component of conditioning at high pulp density which creates a more turbulent conditioning environment, possibly aiding dispersion and/or emulsification of the fatty acid collector.

In the same year as the study by Browning and McVay, Arbiter et al. [12] commented on the poor spodumene selectivity if fatty acids were conditioned at low intensity (rpm) or with short residence times, and high selectivity when conditioned at higher intensity or longer residence times. The initial collector adsorption was postulated to be non-selective and then gradually became more selective with longer conditioning time or intensity. Both parameters impact collector dispersion, which could be related to the formation of the acid–anion complex that drives spodumene flotation. The authors also commented on the scale-up challenges associated with conditioning in spodumene flotation, particularly because the optimal time and agitation impact both physical and chemical pulp conditions. In this study, the best pilot scale conditioning settings were 60% solids, a high mixing intensity (1800 rpm), a moderate conditioning time of 8 min, and a combined power consumption around 16 kWh/t from NaOH scrubbing and conditioning.

In the early 1980s, McDaniel [56,57] attempted to further optimize the spodumene flotation procedure with King’s Mountain ores. Fatty acid conditioning and scrubbing with NaOH were again identified as very important to achieve high concentrate grades and recoveries, and it was proven that frother could be eliminated with a ~30% increase in fatty acid dosage. Performance was best when conditioning pulp density was kept between 60% and 65% solids, with lower concentrate grades reported as density decreased. While this varies from the findings of Browning and McVay, [13] who reported best performances between 40% and 50% solids, there is agreement that higher pulp density produced higher concentrate grades and lower pulp density produced lower concentrate grades. At a constant fatty acid dosage, shorter conditioning times produced high recoveries at lower concentrate grades, while longer times produced lower recoveries at improved concentrate grades. Finally, at higher dosages the recovery was maintained for longer conditioning times at higher concentrate grade, suggesting a combined effect of collector dosage and conditioning time. For all tests, it was reported that flotation performance was maintained if conditioning pH stayed between pH 8.6 and 9.5, although it is unclear if pulp pH was maintained during conditioning, or if this was the initial pH before fatty acid addition [56,57].

The observation by both McDaniel [56,57] and Arbiter et al. [12] that a higher dosage maintained lithium recovery when conditioning time was longer is supported by the theory that an irreversible change in collector speciation occurs during conditioning resulting in decreased spodumene recovery. Because fatty acids are poorly soluble, there is excess liquid molecular acid present in the pulp compared to dissolved ionic species when they are first added to the pulp. When conditioning times are short and there is likely still excess molecular acid in the pulp, lithium recovery is reported to be high but with poor selectivity. As conditioning reaches the optimum time and mixing intensity, more dissolution of collector should occur, which corresponds to an observed increase in concentrate grade at similar lithium recovery. In situations of over-conditioning, the concentrate grade is further increased while recovery decreases, which should correspond to a depletion of liquid molecular acid in the pulp. If this is correct, it would explain McDaniel’s findings

that concentrate grade was maintained at higher collector dosages with conditioning longer times.

Early bench-scale flotation studies identified that the conditioning stage in spodumene flotation with fatty acids is very important for selective recovery and is sensitive to parameters like pH, pulp density, conditioning time, and collector dosage. However, the observed phenomena in historical research are lacking a fundamental explanation. Further testing is required to better identify how conditioning components like pulp density, conditioning time, and mixing intensity during conditioning impact collector speciation and ultimately, flotation performance.

Alternate Flowsheets for Spodumene Concentration

In 1953, Banks et al. [112] presented a method of reverse gangue flotation to produce spodumene concentrates from North Carolina ores. Caustic starch or dextrin was used to depress spodumene and Fe-bearing silicates, and a cationic amine collector was added to float quartz, feldspar, and mica together at high pH (up to 11.5). The rougher tailings, or spodumene concentrate, contained nearly all Fe-bearing silicates as these minerals (hornblende) are closely related mineralogically to spodumene. To remove these, the pulp was conditioned at high-density with HF, then floated at 25% solids with a sodium resinate collector. The process was confirmed at pilot scale and produced concentrates grading above 6.1% Li₂O and 71% lithium recovery. Goter et al. [113] described the spodumene reverse-gangue flotation flowsheet used by Foote Mineral Co. after they acquired the property from Solvay. The flowsheet was like that of Banks et al. [112] and was used at Foote Mineral Co from 1951 until 1953 when it was replaced by direct spodumene flotation with a fatty acid collector, which resulted in improved lithium recoveries and better plant control [20].

Spodumene deposits can contain beryl (Be₃Al₂(SiO₃)₆) as a valuable by-product, however, selective separation is difficult as both minerals are susceptible to adsorption of fatty acid collectors at cationic Al³⁺ surface sites. Browning et al. [20] depressed beryl during spodumene flotation by conditioning the feed at pH 6.5 with a combination of sodium lignin sulfonate and sodium fluoride (NaF) before oleic acid addition. Not only did these reagents depress beryl, but they also allowed for the omission of scrubbing with NaOH. To recover beryl from the tailings, mica was floated at acidic pH, which reversed the beryl depression and allowed for beryl to then be floated with oleic acid collector under similar conditions as upstream spodumene flotation. This scrubbing approach without NaOH also produced good spodumene recoveries and concentrate grades with ores from Bessemer City, N.C., Hill City, S.D., and Val D'or, Q.C., Canada.

The Evolution of Industrial Spodumene Flotation Practice

After 1973, all spodumene at Kings Mountain was concentrated by flotation, when DMS operations ceased [8,114]. Despite testing of a variety of flowsheets, (such as those involving reverse flotation, discussed in the previous section) very few changes were adopted by the 1970s. The flowsheet described is presented in Figure 9 and the specific plant conditions included a grind size of 100% passing 212 µm with a two-stage desliming to remove the −15 µm particles and decrease gangue entrainment to the concentrate. Next, the classified feed was scrubbed with NaOH (not lignin sulfonate and NaF) to activate spodumene surfaces at high pH, then conditioned at neutral pH, 55% solids, and a dosage of 750 g/t TOFA with a glycol type frother. The TOFA used contained about 5%–7% rosin acids. After high density conditioning, flotation was conducted at 30% solids and used two cleaning stages to produce a chemical spodumene concentrate grading 6.3% Li₂O with lithium recovery around 88%. There was also some production of ceramic grade concentrate that required higher Li₂O and lower Fe₂O₃ content, generated through two additional cleaner flotation stages, at a lower final lithium recovery.

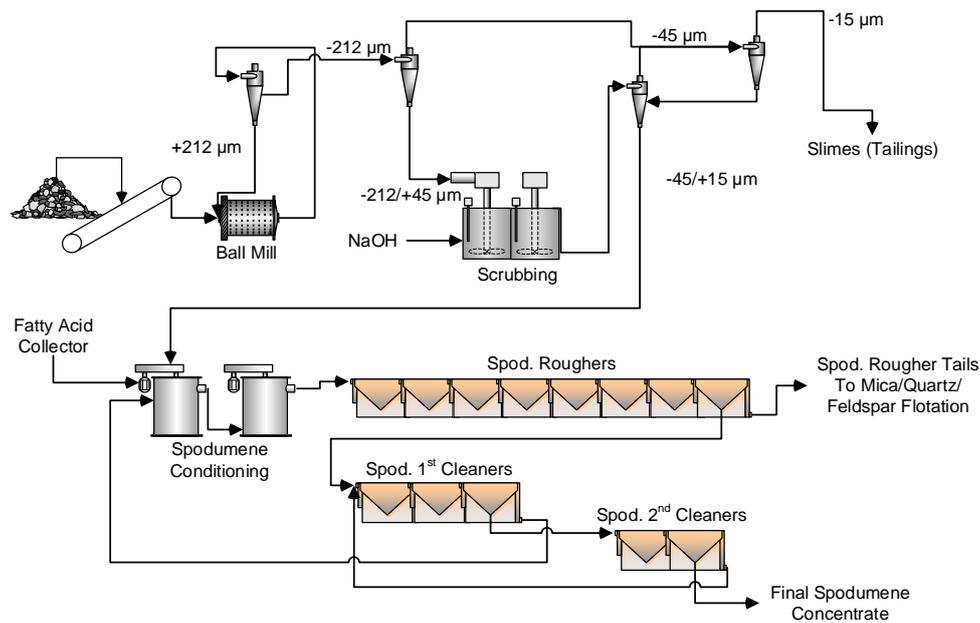


Figure 9. Spodumene flotation flowsheet described by Redeker [8].

In addition to spodumene production from the United States, there was some 20th Century Canadian production by the Tantalum Mining Corporation of Canada (TANCO) operation at Bernic Lake, Manitoba. The deposit is a high-grade pegmatite ore grading around 3.2% Li_2O that contains spodumene and other lithium bearing minerals like amblygonite and lepidolite. The operation produced tantalum until 1982 due to falling demand and prices and ultimately shifted to production of high-grade ceramic spodumene concentrates grading $>7.1\%$ Li_2O , $<0.3\%$ P_2O_5 , and $<0.08\%$ Fe_2O_3 in 1985 [21]. Production of spodumene concentrates from this material was first investigated through a reverse gangue flotation process developed by the Canadian Centre for Mineral and Energy Technology (CANMET) and a direct anionic flotation method developed by Lakefield Research. The process commissioned in 1985 was an adaptation of the anionic flotation process developed at Lakefield Research. Direct spodumene flotation was achieved with a mix of oleic acid and petroleum sulfonate as an anionic spodumene collector. Magnetic separation was required to meet the target iron levels. Amblygonite pre-flotation was eventually introduced to reduce P_2O_5 content since amblygonite typically reported to the spodumene concentrate making it difficult to meet target P_2O_5 levels. This was achieved by depressing spodumene with starch and using starvation levels of the same collector blend. If properly dewatered to remove the starch before high-density conditioning, spodumene flotation was not impacted [21]. Burt et al. [21] reported typical rougher flotation lithium recoveries around 92% with final 3rd cleaner flotation recoveries around 82%. About 9.5% of the lithium distribution reported to the cleaning stages and about 3% of the lithium distribution reported to the rougher tails. Spodumene production at TANCO continued until 2009 when it was discontinued due to lack of demand but was recently recommissioned by the new owner Sinomine in 2021 [47,115]. For two brief periods in the 2010s, there was some Canadian spodumene production from the Quebec lithium mine (later North American Lithium and now owned by Sayona) by flotation with fatty acids. The initial operation closed in 2014 and was reopened in 2017 as North American Lithium, before closing again in 2019 due to bankruptcy [116].

Australia is home to the largest active spodumene mine in the world at Greenbushes, Western Australia and several other spodumene operations that started production in recent years, but publicly available process information is limited. A 1989 report by Bale and May [93] about the Greenbushes operation indicates the initial procedure used a bulk flotation stage to recover spodumene and tantalum with a fatty acid collector, soda ash

at pH 7.0–7.5, and two cleaner stages, to produce a concentrate grading 7.2% Li_2O and 0.4% Fe_2O_3 . The use of additional frother or NaOH scrubbing was not discussed in the procedure, and it is possible NaOH was not needed due to the quality of the deposit. The bulk concentrate was then scrubbed at low pH with sulfuric acid to remove the fatty acid, before going through gravity and magnetic separation to remove minerals like cassiterite, tantalite, and tourmaline, as well as some iron contamination from the grinding media [94]. Factors like the high 4.0% Li_2O feed grade in the early years of operation, likely allowed for a simplified flowsheet comparable to those used in some of the ‘higher grade’ North American ores [93]. Recent reports put Greenbushes current average feed grade at ~2.8% Li_2O , but a lack of process information makes it unclear if, or how, flotation conditions have changed [38].

It is clear from the available industrial literature that little has changed in spodumene flotation since the first major operations commenced at King’s Mountain. Fatty acids have remained the dominant collectors at dosages from 500–750 g/t and spodumene flotation pH is generally between 7.5 and 8.5. The critical steps for successful industrial spodumene flotation are: (1) the NaOH scrubbing stage to activate spodumene and, (2) the high intensity conditioning stage—that is best when conducted around neutral pH, pulp densities above 55% solids, for around 10 min, and with sufficient collector dosage. There is also some indication that ions naturally present in the water or added by pH modifiers (soda ash) can be detrimental to spodumene flotation performance. The need for NaOH scrubbing in spodumene flotation was described by Moon and Fuerstenau [35] but there has been no fundamental explanation of the mechanisms occurring during high-density conditioning.

3.2.2. Recent Publications (2000-Present)

Industrial Projects

With several new spodumene projects under development companies are keeping specifics about their flotation circuits confidential, which makes it difficult to know how future designs will differ from previous and existing operations. Some information is available in recent National Instruments 43-101 (NI 43-101) Technical Reports from select Canadian spodumene projects. For example, the Nemaska Whabouchi project achieved a final concentrate grade of 6.6% Li_2O and Li recovery of 88.2% with Sylfat FA2 collector, TP-100, sodium silicate, and a high-density conditioning stage in lab scale bench flotation [43]. Locked-cycle test work for the Critical Elements Rose Lithium Tantalum Project achieved 89% recovery at 6.65% Li_2O grade using Sylfat FA2, F220 dispersant, and high-density conditioning at 60% solids. Sylfat FA2 dosages from 770 g/t to 850 g/t were needed across different areas of the deposit, with higher dosages required for reduced feed grades [42]. While this information is limited to lab scale testwork, the conditions are very similar to several of the publications discussed in Section 3.2.1.

Collector Testing

In the past three decades, there were very few studies of fatty acid flotation with real spodumene ores. In 1999, Amarante et al. [117] investigated spodumene flotation from a Northern Portugal ore containing between 1.9% and 3.0% Li_2O . The authors explored collector development by adding various reagents to oleic acid to increase the quality of spodumene concentrates for glass and ceramic applications. Prior to flotation, the feed was ground to 95% passing 300 μm and all particles under 75 μm were removed, which is a coarser cut-size for desliming than other previously discussed procedures. The authors achieved their highest final concentrate grades and recoveries using 500 g/t of oleic acid with an addition of 200 g/t naphthenic acid and 3500 g/t of an unspecified fuel oil at pH 8.5–9.5. The naphthenic acid was used to enhance collector properties—most likely selectivity—but the exact function of fuel oil was not discussed. While performance with this collector mixture looked promising, the results with pure oleic acid, or other collectors, were not presented for comparison. Additionally, high fuel oil requirements in

the optimized collector could be an obstacle for a commercial application when considering the dosages used in other spodumene flotation work.

In 2017, Gibson et al. [118] published a study testing different TOFA collectors on real spodumene ores. In this work, two separate ore composites with varying levels of Fe-bearing amphiboles were used to study the rejection of Fe-bearing silicates through magnetic separation and flotation. The flotation study tested three different TOFA collectors from two different manufacturers (denoted C1 and C2 in Figure 10a,b) to evaluate the impact of rosin content on Fe rejection from the spodumene concentrate. The feed was scrubbed with NaOH and lignin sulphonate, then deslimed to target a particle range of $-300/+15\ \mu\text{m}$, before collector conditioning at 50% solids. The overall flotation results at pH 8.5 can be seen in Figure 10a,b. From left to right, the points represent the rougher, 1st Cleaner, 2nd Cleaner, and 3rd Cleaner concentrates.

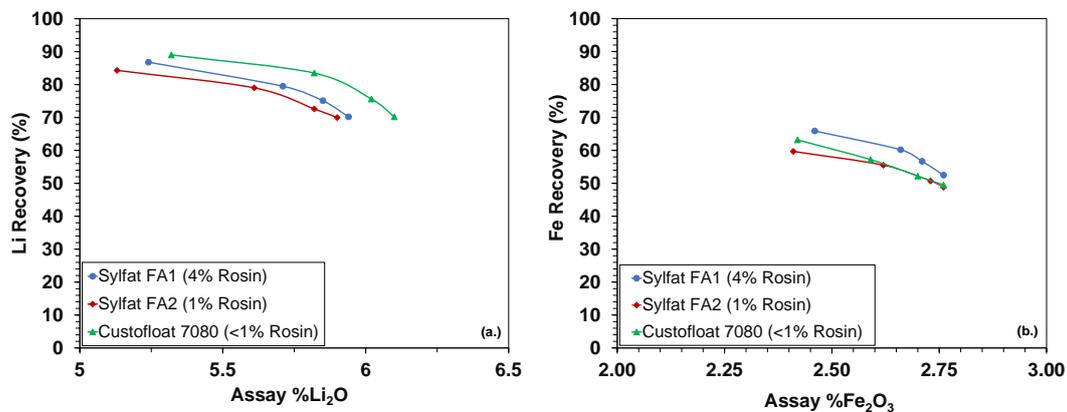


Figure 10. Li₂O (a) and Fe₂O₃ (b) grades and recoveries for three commercial TOFA collectors with varying rosin content, adapted from [118].

The collectors containing 1% or less rosin acid from both suppliers produced lower Fe recoveries with different impacts on Fe₂O₃ grade. The best Li grade and recovery was achieved with the collector containing less than 1% rosin acid, the only collector from the second supplier. The authors commented that the reason for improved selectivity was not fully understood but suggested the change in rosin content may have impacted either the frothing properties, resulting in less hydraulic entrainment, or the collector affinity for certain Fe-bearing silicates. Interestingly, the impact of rosin content on Fe grade and recovery is somewhat consistent between the two suppliers. However, the 1% rosin content with C1 resulted in the poorest Li performance, while the C2 collector resulted in the best performance.

It is possible there is a fundamental difference in rosin properties between the two collector suppliers as this is known to change depending on the geographical location of the pine trees used in TOFA production. While the rosin acid content in TOFA collectors has been discussed by other researchers for their impact on froth properties, these rosin contents are often much higher than 4% [9,19]. For example, a scheelite flotation study by Filippov et al. [19], found that as the rosin acid content in an oleic/linoleic acid collector increased the recovery increased, but selectivity decreased. It was determined that the carboxylic acid group of the rosins absorbed unselectively at Ca²⁺ mineral sites, decreasing selectivity between common Ca-bearing minerals like scheelite and calcite in this system. This may also contribute to poor selectivity in spodumene flotation, but in the case of spodumene and the selective rejection of Fe-silicate gangue, it is unclear if rosin acids impact collector interactions with Al and Fe cationic sites. Although there was a clear impact of rosin content on the Fe response in spodumene flotation presented by Gibson et al. [118], further explanation of the mechanism responsible for the improved selectivity is needed.

Based on the existing hematite literature, the pH range and adsorption mechanism of fatty acids onto Al^{3+} and Fe^{3+} sites are very similar and both minerals float readily between pH 7 and 9 [36]. Unfortunately, the similar adsorption behaviour between Al sites on spodumene and Fe sites on hematite suggests that it will be difficult to selectively reject Fe-bearing silicate gangue with fatty acids if iron is present as Fe^{3+} . This becomes further complicated when several of these gangue minerals also contain aluminum and have similar Al^{3+} adsorption sites as spodumene. It may be possible to perform a pre-flotation stage to selectively remove Fe bearing minerals while depressing spodumene—like the amblygonite pre-flotation implemented at the older TANCO operation—but this will require further investigation and a selective depressant.

To supplement a fundamental study with a mixed anionic/cationic collector blend, Xu et al. [58] tested a 9:1 NaOl/DTAC (dodecyl trimethyl ammonium chloride) blend at 800 g/t on spodumene ore sample (1.43% Li_2O) from the Jaijika Lithium Mine in Sichuan, China. The authors compared flotation performance to that with a collector blend of oxidized paraffin wax soap (2000 g/t) and naphthenic soap (400 g/t) and reported an increase in lithium recovery from 80% to 85% and an increase in concentrate grade from 5.9% Li_2O to 6.2% Li_2O . There was no direct comparison between the NaOl/DTAC blend and pure NaOl or oleic acid, so it is unclear how performance would compare with traditional fatty acid collectors. According to the authors, the oxidized paraffin wax soap and naphthenic soap collector blend was the collector used in the original plant set up, but no reference was provided so it is difficult to determine how this blend was developed and why such high dosages are needed. Unfortunately, aside from collector dosage, there was no further discussion of flowsheet design or flotation conditions like pulp pH [58].

Flotation Optimization Studies

In another example, Menéndez et al. [119] investigated the optimization of spodumene recovery with an ore from Pontevedra, Spain (1.85% Li_2O). Feed was ground to a 100% passing size of 400 μm with NaOH as the pH modifier and a pine oil frother. The authors evaluated the impact of several variables on the rougher Li_2O grade and recovery, including oleic acid dosage, pulp pH, conditioning time, temperature, and pulp percent solids. The performance at the determined optimized conditions was 96.9% rougher lithium recovery at a 4.2% Li_2O rougher concentrate grade using 1400 g/t oleic acid at pH 7.5. Spodumene recovery decreased as pH dropped below 7 with similar concentrate grades and remained high when above pH 10, but with low concentrate Li_2O grades. An increase in conditioning time from 1 to 20 min at pH 7.5 resulted in a significant increase in concentrate grade from 4.2% Li_2O to 5.2% Li_2O with only a 4% decrease in Li_2O recovery. This agrees with observations from spodumene work by Arbiter et al. [12] and McDaniel [56,57] regarding long conditioning times, and it is likely that the higher collector dosage may have helped to maintain lithium recovery while grade improved. Similar decreases in recovery at long conditioning times have been discussed in hematite flotation by Quast [28], but in this case, the author postulated that the decrease in recovery was related to a build-up of slimes, not changes in collector speciation or the formation of the acid-oleate complex.

Conditioning at high temperatures resulted in high recovery and poor selectivity, which suggests that there was an increase in collector solubility at temperatures above 50 °C and a potential change in speciation behaviour. The results at higher temperature were like those when operating at high pH, which indicated increased collector adsorption onto gangue particles. The conditions used by Menéndez et al. differed from historical procedures; in particular, the optimum percent solids was about 18%, which is considerably different from prior studies which indicated optimal conditioning at 50% solids or greater. Although rougher recovery was high, the rougher concentrate grade reported by Menéndez et al. was considerably lower than that reported in past studies. At lower dosages (~350 g/t), the authors reported a lithium recovery of about 81% at a higher grade of 5.6%, so the determined optimal dosage (1400 g/t) likely improved recovery but sacrificed grade. The choice to condition at 18% solids may have also contributed to poor concentrate

rougher grade, as higher percent solids during conditioning has been shown to produce higher concentrate grades.

Cao et al. [120] published the most recent study with a real spodumene ore grading 1.68% Li_2O , which investigated the impact of water hardness (Ca^{2+} and Mg^{2+}) on spodumene rougher flotation. The authors performed three separate four-factor central composite experimental designs to evaluate the impact of different dosages of pH modifiers soda ash and NaOH, the collector NaOl, and cationic activator CaCl_2 with three water samples of varying hardness (56 mg/L, 421 mg/L, and 790 mg/L). Flotation was conducted at 30% solids and there was no discussion of NaOH scrubbing, high pulp density during conditioning, or target pulp pH, but it is assumed pulp pH would differ depending on NaOH and soda ash dosage. The best performance was achieved with the lowest water hardness sample at 73.1% lithium recovery and 4.46% Li_2O rougher concentrate grade, using the conditions: 1356 g/t NaOl, 51 g/t CaCl_2 , 693 g/t NaOH, and 318 g/t soda ash. At a water hardness of 421 mg/L the lithium recovery was 70.7% at a 3.9% Li_2O grade; this required an increase in NaOl dosage and soda ash to 1733 g/t and 900 g/t, respectively, with less NaOH (126 g/t) and no activator. The increased NaOl and soda ash dosages were thought to offset reactions with Ca^{2+} in solution. Finally, the hardest water (790 mg/L) required the highest dosages of NaOl, NaOH, and soda ash of 2100 g/t, 900 g/t, and 900 g/t, respectively, and produced the worst grade and lithium recovery at 1.66% Li_2O and 67.2%, respectively. The hard water results align well with the earlier work of Munson and Erickson [91] and suggest a high concentration of cations in solution is detrimental to selectivity in spodumene flotation.

The best rougher flotation performance achieved by Cao et al. [120] was considerably lower than other studies of spodumene flotation using similar grade ores. Aside from the scrubbing and conditioning, one major difference was the collector used. In older publications, molecular fatty acids like oleic acid or TOFA were used and produce high grade spodumene concentrates with high recoveries using dosages around 500 to 1000 g/t, but they require high density conditioning to overcome poor solubility. In the study by Cao et al. [120], NaOl (the Na-salt of oleic acid) was the collector, which has different solubility properties than traditional fatty acids, and may have impacted the flotation performance with the low water hardness sample. Any difference in the collector adsorption process between NaOl and oleic acid onto spodumene are not clear, but the industry would likely benefit from a better understanding of this to better connect the results of fundamental studies and the industrial practice in spodumene flotation.

3.3. Fundamental Investigations to Improve Spodumene Flotation

As discussed in Section 3.1, fundamental single mineral studies are a common method used to understand and isolate the flotation mechanisms in froth flotation. In recent spodumene literature, inconsistent flotation performance has been reported when pure NaOl is used under flotation conditions like those described by Moon and Fuerstenau [35], but without NaOH scrubbing. These inconsistencies have led many researchers to investigate the use of mixed anionic/cationic collectors and cationic activators to improve spodumene recovery. At this point, nearly all testwork in this area has focused on single mineral systems and further work will be needed before industrial application.

3.3.1. Mixed Anionic/Cationic Collector Systems

In the past decade, one of the most popular approaches improving spodumene flotation has been the combination of cationic and anionic fatty acid collectors. Work published by Xu et al. [58] used single mineral studies, and later a real ore system (briefly discussed in Section 3.2.2), to investigate the benefit of a mixed anionic and cationic collector. Initially, microflotation tests were conducted to determine the optimum molar ratio of NaOl and dodecyl trimethyl ammonium chloride (DTAC) to recover spodumene and depress feldspar. The ideal ratio was then tested with a real ore system. The authors also investigated the impact Ca^{2+} as an activator, NaOH pre-treatments, and soda ash as a feldspar depressant

with the new collector blend. The best NaOl:DTAC ratio was reported to be 9:1 at a combined collector concentration of 4.0×10^{-4} M. As presented in Figure 11, the maximum spodumene recovery with this blend was around 85% at pH 8.5, a significant jump from about 56% recovery with pure NaOl. Calcium as an activator increased spodumene recovery to over 90% at around pH 12, but it was detrimental to feldspar rejection; feldspar depression required the addition of soda ash. The high recovery using a calcium activator at high pH indicates a strong interaction between the Ca^{2+} ion and the oleate monomer or dimer, but not the acid-oleate complex present at lower pH.

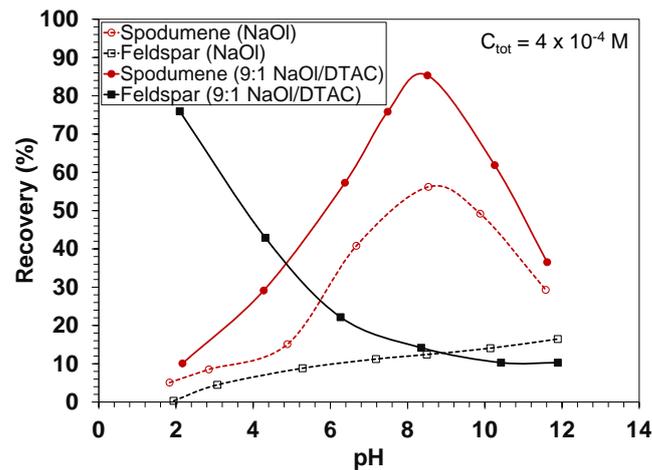


Figure 11. Spodumene recovery for mixed NaOl and DTAC collector system, adapted from [58].

NaOH pre-treatments of spodumene particles prior to flotation with the 9:1 NaOl/DTAC collector blend produced higher spodumene recovery and lower feldspar recovery. NaOH is often used in spodumene flotation during a pre-treatment stage to reveal active cationic Al sites for anionic collector adsorption. In theory, this NaOH treatment should only improve the chemisorption of the anionic collector onto spodumene and there should be little impact on the interaction of DTAC, as the cationic collector molecule of DTAC has been shown to adsorb onto negatively charged particle surfaces [35,59]. Testing with NaOH and only NaOl as the collector was not reported in this study so it is unclear how it would compare to NaOl/DTAC. As noted, testing with a real ore determined 800 g/t NaOl/DTAC improved flotation performance from the original plant collector (2400 g/t oxidized paraffin wax soap and naphthenic soap blend), but there was no direct comparison to NaOl or pure fatty acids [58].

Other authors have also used mixed anionic and cationic collectors in single mineral flotation with feldspar and spodumene. Tian et al. [98] expanded on the NaOl/DTAC study, using FTIR measurements to determine the collector interaction. It was concluded that spodumene floatability was improved by the adsorption of NaOl onto the spodumene Al sites, followed by the formation of an electroneutral DTAC-NaOl complex that co-adsorbed at the stern layer. Wu et al. [99] explored the blend of the cationic collector tributyl tetradecyl phosphonium chloride (TTPC) and NaOl in spodumene feldspar separation. With a combined collector dosage of 4.0×10^{-4} M, the authors determined the optimum molar ratio of NaOl:TTPC to be 5:1, with a maximum selectivity at pH 4. Under these conditions, spodumene recovery was at 75%, while feldspar recovery was around 5%.

The results from Wu et al. [99] saw improved selectivity of spodumene recovery from feldspar, but the feldspar response appears to be strictly dictated by the presence of TTPC in solution with little impact from NaOl at any pH. In addition, the small portion of TTPC causes a significant shift in pH for spodumene recovery from pH 8.5 to pH 4, bringing to question the contribution to recovery from NaOl under these conditions. From the literature discussed, it would be expected that operating at pH 4 results in a low concentration of the anionic oleate species responsible for collector adsorption on spodumene surfaces and a

poor flotation response. The authors did not comment on the typical doses of TTPC when used individually as a collector.

Works by Xie et al. [101,102,104,105] represent some of the few instances of fatty acids other than NaOl being used in spodumene flotation. The authors tested combinations of α -bromododecanoic acid (α -BDDA, a C₁₂ fatty acid with a bromo-substituent at the 12-position) and the cationic collectors decyloxy-propyl-amine (DPA) and dodecylamine (DDA). Pure samples of spodumene and feldspar were used for single mineral microflotation and FTIR, XPS and Zeta potential measurements. In a 2020 α -BDDA/DPA study, recoveries of both minerals were above 90% with pure DPA pH 11, while pure α -BDDA resulted in little recovery of either mineral at any pH. The authors reported the best possible selectivity was 80% spodumene recovery and 30% feldspar recovery at pH 4.5, using DPA and BDDA combined at a molar ratio of 1:1.

Different results were published by the same authors in a 2021 study combining DDA with α -BDDA. The authors found the optimum molar ratio of α -BDDA:DDA to be 19:1 and using this blend at a concentration of 2.1×10^{-4} M produced around 65% spodumene recovery and 5% feldspar recovery. Spodumene recovery then increased above 85% with a higher collector concentration of 5.0×10^{-4} M [102]. It is likely the increased α -BDDA concentration in the 2021 study was the main source of improved spodumene recovery, and the DDA component had little impact. This is an order of magnitude higher in collector concentration, and a change of this degree in NaOl concentration can result in a significant increase in spodumene recovery as indicated by Moon and Fuerstenau [35]. A follow-up investigation into the performance of pure α -BDDA as a spodumene collector could be beneficial as would a direct comparison to NaOl or fatty acid collectors.

In response to poor performance and selectivity in microflotation with pure NaOl as the collector, several studies have resorted to mixed anionic and cationic collector systems to recover spodumene and depress feldspar. While successful in single mineral systems, these blends have not been tested on real ore systems and most authors appear to overlook a key component in spodumene activation for fatty acid flotation—NaOH scrubbing—which may change the performance with pure NaOl. The performance of mixed collector systems can vary, with some systems being driven by the fatty acid component and others by the cationic collector. However, the tendency for cationic collectors to recover both value and gangue minerals with negative surface charges, like spodumene, feldspar, and quartz, could present an obstacle for commercial implementation.

3.3.2. Cationic Activators

The addition of metal ions as activators is a common technique used in flotation to enhance collector adsorption onto particle surfaces. In spodumene flotation, several authors have investigated the use of cationic metal activators to improve interaction with the anionic collectors. In 2014, Yu et al. [121] added Ca²⁺ ions to activate spodumene and determined the 12.3 was the optimum pH for Ca²⁺ activation at a collector concentration of 7×10^{-4} M NaOl. Density functional theory (DFT) calculations from this work determined Ca(OH)₂ to be the primary calcium species responsible for enhancing NaOl adsorption, as this was the stable Ca species on the spodumene surface at pH 12.3. In the same year, Jie et al. [96] reported the addition of Fe³⁺ ions at a collector concentration of 2.0×10^{-4} M NaOl improved spodumene, albite, and quartz recovery from under 10% for all minerals, to 70%, 30%, and 30%, respectively, but at a pH around 7 to 7.5. A follow-up study looked at the impact of Ca²⁺ and Mg²⁺ ions in spodumene flotation at a collector concentration of 6.0×10^{-4} M NaOl. Aligning with the findings of Yu et al., maximum spodumene recovery in this study increased from 10% at pH 8.5 without activators, to around 80% at pH 10 and 83% at pH 12.6 using activators Mg²⁺ and Ca²⁺, respectively [97].

Referencing the findings of Liu et al. [97], Filippov et al. [95] used Ca²⁺ activators and 250 mg/L or 8.2×10^{-4} M NaOl to float two spodumene size fractions, +40/−80 μ m (fine) and +80/−150 μ m (coarse), to capture the impact of particle size on flotation response. Without activators, peak recovery for the fine and coarse fractions

was 75% and 60%, respectively, at pH 10. With activators, the recovery in the coarse fraction increased to 85% above pH 10, while fine fraction exhibited recoveries around 90% from pH 4 to pH 10. Gao et al. [122] used single mineral microflotation to demonstrate that in addition to being activators, Ca^{2+} cations form complexes in solution with oleate that strongly adsorb onto spodumene and render the mineral hydrophobic. Another recent study by Zhang et al. [123] developed an explanation as to why Ca^{2+} ions are often required to float spodumene despite the high concentration of Al sites. DFT calculations indicated the interaction of oxygen from water with surface Al sites, weakens the adsorption strength of NaOl. It is unclear if this differs with NaOH pre-treated spodumene, as this was not an aspect of this study. In general, it appears that the use of NaOH pre-treatments in spodumene research was often overlooked when cationic activators were used. However, this is an important step in spodumene flotation as it provides more cationic Al adsorption sites for the fatty acid anion which is vital for good flotation performance. A 2020 study by Zhu et al. [59] indicated that the spodumene recovery from a synthetic mixed mineral system, using pure NaOl and no activators, increased gradually from 30% to about 70% when NaOH scrubbing dosage was increased from 0 to 1500 g/t. As lithium recovery increased, the concentrate grade also increased from about 5.8% Li_2O to about 6.2% Li_2O . Thus, it is possible that alkaline scrubbing with NaOH will yield similar improvements in spodumene recovery as cationic activators while improving selectivity.

A molecular dynamic simulation study of spodumene in saltwater out of Chile, reported the combined adsorption of several alkali and alkaline cations (Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ , Mg^{2+} , Ca^{2+} , Sr^{2+}) onto spodumene would hinder fatty acid adsorption at pH 8 [124]. This observation tends to align with observations made in laboratory flotation with real spodumene ores which reported poor recovery and selectivity at high water hardness levels.

Although cationic activator studies do little to discuss selectivity, they can provide insight into the behaviour of oleate interaction. Except for the fine fraction in the final example by Filippov, the use of Ca^{2+} and Mg^{2+} ions to improve spodumene recovery required an operating pH > 10. At this alkalinity, collector adsorption should occur as chemisorption between the cationic activator and the oleate anion or dimer; and adsorption of the acid-oleate complex is unlikely due to its low concentration at high pH. Interestingly, the improved spodumene recovery with Fe^{3+} ions reported by Jie et al. [96] resulted in little change in pH when compared to flotation with only oleate, at a slightly alkaline pH between 7 and 8.5. Without activators, there was chemisorption of an acid-oleate complex at the Al^{3+} surface site, and this same species is likely responsible for interaction with the Fe^{3+} activators. This is supported by the fact that spodumene and Fe-bearing gangue minerals float under the same conditions with fatty acid collectors.

The pH range of oleate chemisorption onto spodumene with different activators suggests the fatty acid-anion complex prefers cationic sites with higher oxidation states like Fe^{3+} and Al^{3+} , while the anion preferentially interacts with Mg^{2+} and Ca^{2+} sites. A closer look at the interaction of different oleate species in other mineral systems with a variety of cationic surface sites supports this conclusion. Research by Jie et al. [125] confirmed the tendency of oleate to adsorb at different cationic metal sites (Mg^{2+} , Ca^{2+} , Fe^{3+} , and Ti^{3+}) on the surfaces of ilmenite (FeTiO_3) was pH dependent. The ilmenite samples contained varying amounts of Ca and Mg within the crystal structure and strong oleate adsorption was reported across all pH ranges. At neutral to slightly alkaline pH, oleate adsorption was highest at Fe^{3+} and Ti^{3+} sites with high recovery, but as the pH increased, adsorption at Fe^{3+} , and Ti^{3+} sites decreased and adsorption onto Mg^{2+} and Ca^{2+} sites increased; recovery was only maintained for the sample with high Mg and Ca content [126]. This same transition of oleate adsorption site (from Fe^{3+} , and Ti^{3+} to Mg^{2+} and Ca^{2+}) at increased pH was also reported by Liu et al. [125].

While there is a significant amount of spodumene flotation research available, the evidence indicates that there have been no major changes to the fatty acid flotation process since the 1940s. With the use of NaOH scrubbing, high-density conditioning at longer

residence times and higher intensities, and flotation at pH 7.5–8.5, high spodumene recoveries and high-quality concentrate grades can be produced. In contrast, except for Moon and Fuerstenau, most fundamental studies report poor spodumene recovery with NaOl as a replacement for a fatty acid collector. These findings have led to the study of mixed collector systems and cationic activators, that have shown some success, but only in fundamental mineral systems. In real ore systems, these approaches may face issues, particularly since selectivity is reported to be poor with high water hardness and cationic collectors are used in direct flotation of the same gangue silicate minerals found in spodumene ores. The differences between findings with fatty acids in real ore flotation and NaOl in fundamental studies suggest that there is a knowledge gap in the current understanding of spodumene flotation. One major area that would benefit from further study is the high-density conditioning stage. The mechanical and chemical components of conditioning likely have a combined effect that are essential to successful spodumene flotation that cannot be captured in NaOl studies. If fundamental studies can explain how collector adsorption occurs in this stage, it could allow for better control of the conditioning stage and greatly benefit developing spodumene projects.

4. Conclusions and Summary of Research Gaps

Improving selective gangue rejection in spodumene flotation will benefit from a better understanding of fatty acid collector properties and their mechanisms. As discussed throughout this review, NaOl and oleic acid are the focus of most spodumene flotation research, but they have different solubilities and reported flotation performance. The importance of collector concentration and speciation in maximizing desired collector adsorption and frothing behaviour was evident from the available literature. However, it is unclear how collector adsorption and frothing behaviour differs between real ore systems using fatty acids (requiring high-density conditioning) and fundamental studies using NaOl. There is agreement that a peak in ionic activity occurs in oleate solutions around pH 8.5 where the total concentration of oleate anion, dimer, and acid–oleate complex is near a maximum, coinciding with peaks in foaming behaviour and the observed ideal operating pH regions for the flotation of spodumene, as well as other minerals like hematite and ilmenite. Because of their different compositions, it is difficult to know how species distribution differs with TOFA collectors and how the presence of rosin acids impact collector adsorption and froth properties. Further investigations are needed to understand this.

While there is some disagreement on the pK_a values of fatty acids, the understanding of collector speciation is well aligned with spodumene flotation behaviour. In commercial operations, the use of high-density conditioning may help to overcome the poor solubility of fatty acids. In addition to improving solubility, high-density conditioning may also promote the formation of the acid–anion complex, resulting in good selectivity and high spodumene recovery. In contrast, if increasing pH or temperature are used to improve solubility, recovery will be high but selectivity will be very poor as the presence of insoluble molecular fatty acid is needed to promote selective flotation of spodumene.

Research in spodumene flotation has determined that the acid–anion complex is the main ionic species responsible for recovery between pH 7 and pH 9 through chemisorption onto Al^{3+} surface sites. The concentration of Al^{3+} sites is naturally highest on the [110] cleavage plane and can be further increased on all planes through surface treatments with NaOH. Some mixed anionic/cationic collector systems have improved spodumene recovery and selective feldspar rejection, but further research should be conducted with real ore systems as high gangue recovery is possible with cationic collectors. The use of ionic activators like Mg^{2+} and Ca^{2+} was shown to improve spodumene recovery at pH 10 or higher, but could present a similar challenge through inadvertent gangue recovery as is observed when hard water is used in spodumene flotation.

Throughout this review, the different interactions of fatty acid collectors as a function of pulp pH and the cationic species of the adsorption site Mg^{2+} , Ca^{2+} , Al^{3+} , Fe^{3+} , and Ti^{3+} has been discussed. A superimposition of these pH ranges onto the species distribution

diagram is presented in Figure 12, clearly highlighting which species will interact under given pH conditions.

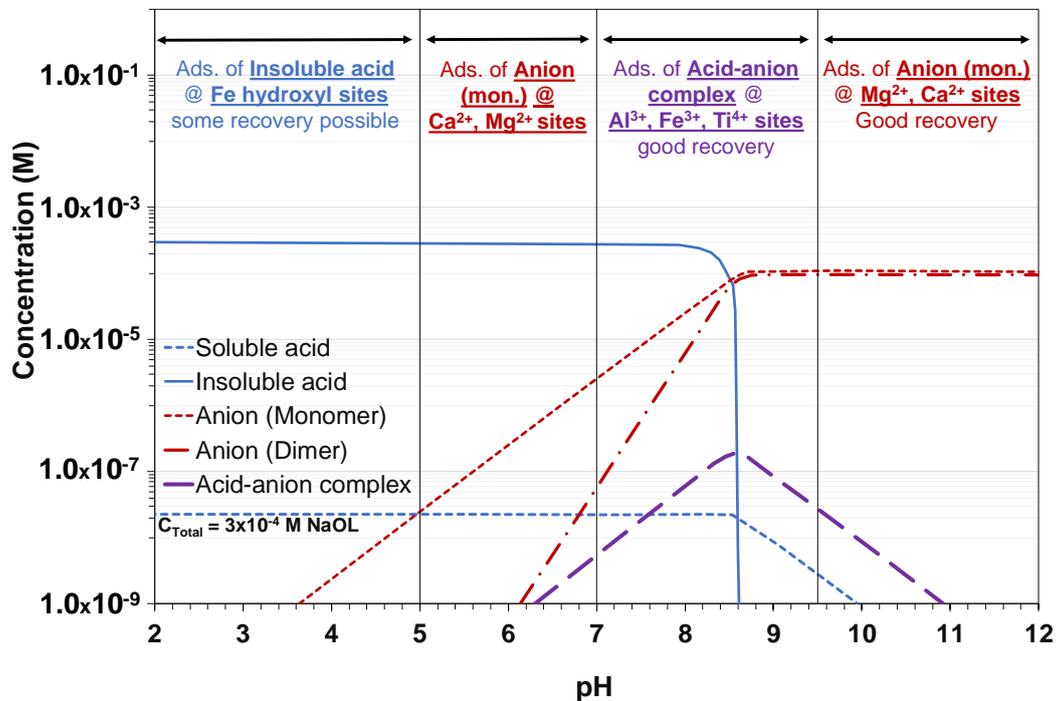


Figure 12. Superimposition of the reported pH ranges for oleate adsorption at different metal sites onto the species distribution diagram for NaOl at 3.0×10^{-4} M, adapted from [14].

From the literature, it is understood that the adsorbed oleate species also depends on the oxidation state of the metal site, as shown in Figure 12. This diagram helps to understand potential interactions that may occur given the pH and metal species on the mineral surface. For example, separation of calcite and other minerals from spodumene should be possible at neutral/slightly acidic conditions, or at highly alkaline conditions. However, the selective separation of spodumene from Fe-bearing gangue minerals may be challenging as collectors adsorb onto Fe surface sites in the same pH region.

5. Future Work

With the increasing mineralogical complexity of new spodumene deposits and lower head grades, there is a pressing need for improving collector selectivity. Investigations should consider the steps used in successful industrial spodumene flotation like NaOH scrubbing and high-density fatty acid conditioning. Future research should focus on further defining the behaviour of anionic collectors at different pH, concentration, and temperature under different mechanical/hydrodynamic conditions (mixing intensity, pulp density) to better understand the mechanisms in industrial spodumene flotation. The industry should also strive to improve understanding of the impact of rosin acid content, different types of fatty acids, and the use of additives in fatty acid collectors on collector-particle interactions, all of which would help collector manufacturers meet the needs of a changing lithium industry. Future spodumene flotation research should work to bridge the current gap between fundamental studies and industrial spodumene flotation processes to de-risk the many developing spodumene projects required for a net-zero future.

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