**Lithium Recovery from Low Grade Resources**

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**Abstract**

The purpose of this project is to develop an effective separation technique which can ultimately process low grade lithium ores into a higher grade lithium product. Spodumene, lithium aluminum silicate, was collected from some mines located near Keystone, South Dakota. One sample was used to find the contact angle of spodumene while the rest was crushed and filtered to obtain a -48+100mesh fraction material size particles. X-ray diffraction demonstrated that the samples were essentially pure spodumene. The crushed spodumene was separated into 1 gram sized portions and then floated using different concentrations of sodium oleate. From concentrations of 0.001-0.004 M there is a good correlation between the percent recovery of spodumene and the contact angle of spodumene. However, at the extreme ends of the concentrations used for flotation, the recovery significantly declined, while the contact angle remained relatively high. The extreme low and high concentration contact angles were unexpected and could be due to surface roughness and or precipitation of metal oleate species at the mineral surface.

1. **Introduction**

Lithium has the potential to be very important in the future industry, especially in rechargeable batteries. (National Research Council of the National Academies, 2008) It is also used as an addition to glass and ceramic bodies. The presence of lithium lowers melting points of certain processes or increases the cooling rate in others, and reduces the coefficient of thermal expansion and viscosity of certain materials. Thus lithium is very helpful in reducing toxic chemicals and contributing to energy savings for production and manufacturing. Lithium can be found in spodumene, which is lithium aluminum silicate, LiAl(Si­2O6), and contains around 8% Li2­O (very rich for a natural source). (Sousa, 2007)

Manganese is a very important metal in industry and is rapidly growing in demand while its supply growth is not enough to satisfy the demand. This has caused the price of manganese to increase over the years, in particular from $1.3 in April 2010 to $1.55/lb in June 2011, which is a 19% increase in 14 months. (Xignite, 2008) In more recent years, the need for manganese arose mainly from the production and consumption in the steel and aluminum industries, especially in China. Because of this increasing demand, alternative processes must be found to identify and produce high grade manganese economically. (Zhang, 2007) There are also no companies in North America that recover manganese, so the United States steelmakers are solely dependent on foreign sources for their manganese requirements. (National Research Council of the National Academies, 2008)

One type of separation process that can be used to obtain a higher recovery of lithium from natural resources is froth flotation. Froth flotation is a process for separating [minerals](http://en.wikipedia.org/wiki/Minerals) from [gangue](http://en.wikipedia.org/wiki/Gangue) (unwanted material) by controlling their [hydrophobicity](http://en.wikipedia.org/wiki/Hydrophobicity). Through the use of surfactants and wetting agents, the hydrophobicity differences between the desired minerals and the waste gangue are increased. It is possible for complex ores to be economically and selectively separated through this process. (Fuerstenau, 1985)

1. **Broader Impact**

In order to reduce the United States’ dependency on foreign resources and increase local production, effective methods of local recovery of manganese and lithium can be developed. This will also help lower the prices of the materials produced with lithium or manganese because local production will not have an imported materials tax and the shipping costs for manganese and lithium will be greatly reduced.

1. **Procedure**

**3.1 Materials**

Manganese-bearing nodules are known to exist in the Chamberlain, South Dakota area. During a trip to that area samples were obtained and returned to South Dakota School of Mines and Technology for experimentation. (Figure 1)



Figure 1: Manganese-bearing sea nodule samples

Lithium-bearing spodumene can be found in several mines in Keystone, South Dakota. Spodumene samples were taken from some of these mines for analysis and experimentation. (Figure 2)



Figure 2: Lithium-bearing Spodumene samples

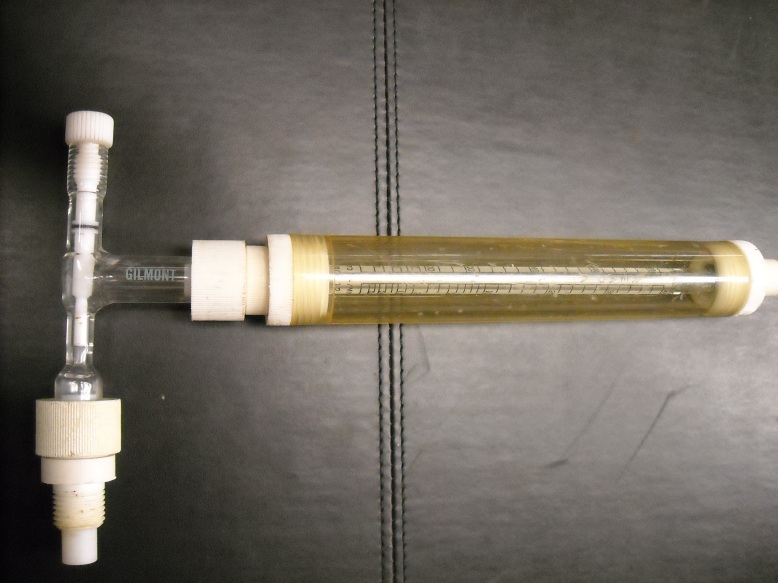
**3.2 Equipment**

The following equipment was used for the flotation experimentation:

1. Figure 3: Hallimond tube flotation cell

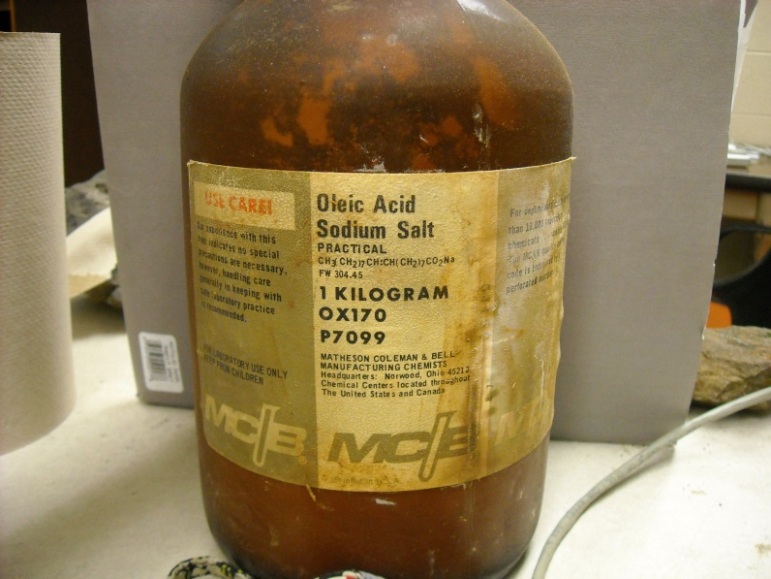


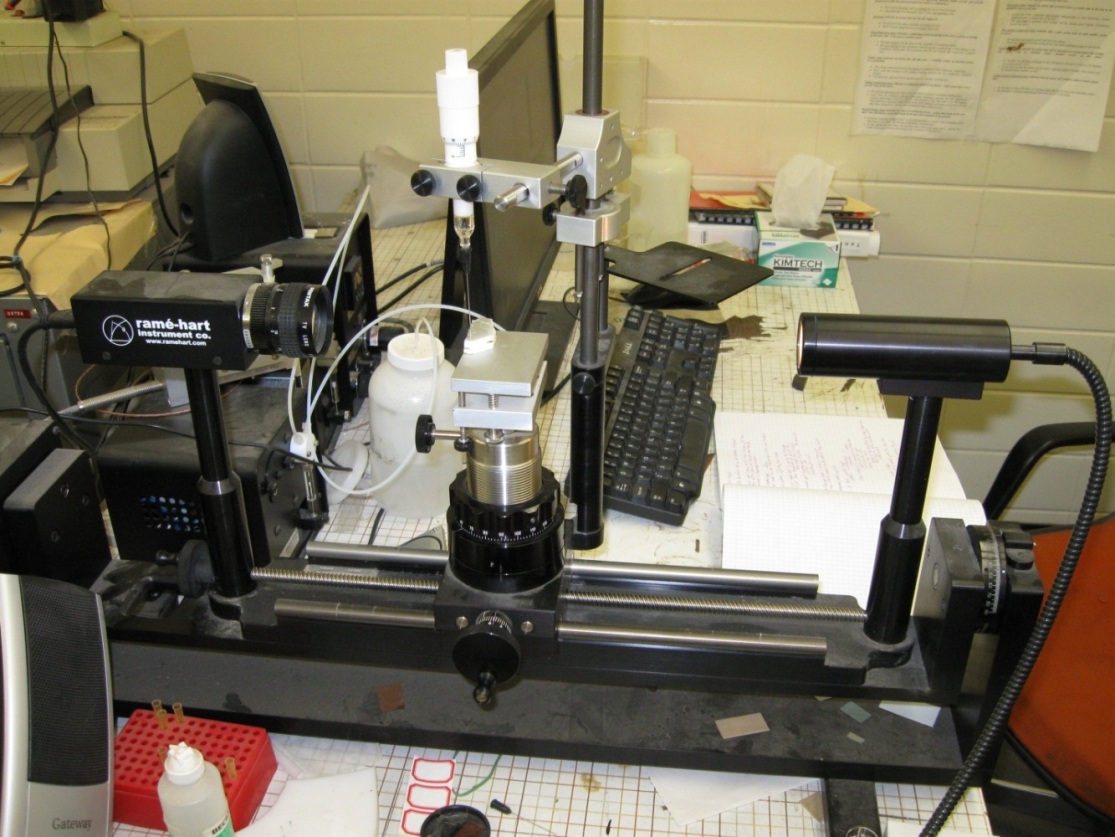
1. Figure 4: Nitrogen flow meter



1. Figure 5: Tygon tubes for nitrogen flow



1. Figure 6: Sodium oleate ≥99%, C18H33NaO2
2. Sodium hydroxide, NaOH, and hydrochloric acid, HCl
3. Figure 7: Ramé-Hart Model 500 Advanced Goniometer Tensiometer with DROP image software



1. Figure 8: Ohaus Moisture Determination Balance with Oven



1. X-ray diffraction instrument, Rigaka Model
   1. **Experimental Procedure**
      1. **Polishing and Contact Angle**

Nodule samples appearing to contain higher amounts of manganese were selected and polished to have two flat, parallel sides using grinder-polisher machines up to 0.3 microns. This was also done for the spodumene sample. Both samples were rinsed with tap water, brushed with nylon brushes, and left to dry (Figure 9).



Figure 9: Polished manganese nodule and spodumene samples

The contact angles of these samples were measured using a contact angle goniometer (Figure 7). With this instrumentation, a 10µL drop of deionized water at pH 9 was carefully placed on the flat surface of the sample, such that it could be seen by the camera on the screen. The drop image program was used to determine the angles of the right and left sides of the droplet in the image once a second for ten seconds. The mean of these angles was calculated and recorded as well as the height and width of the droplet over this period of time. This was done several times for deionized water and different concentrations of sodium oleate in order to understand the variability in the contact angle measurements and see how these measurements change with respect to concentration.

* + 1. **Preparation of Spodumene**

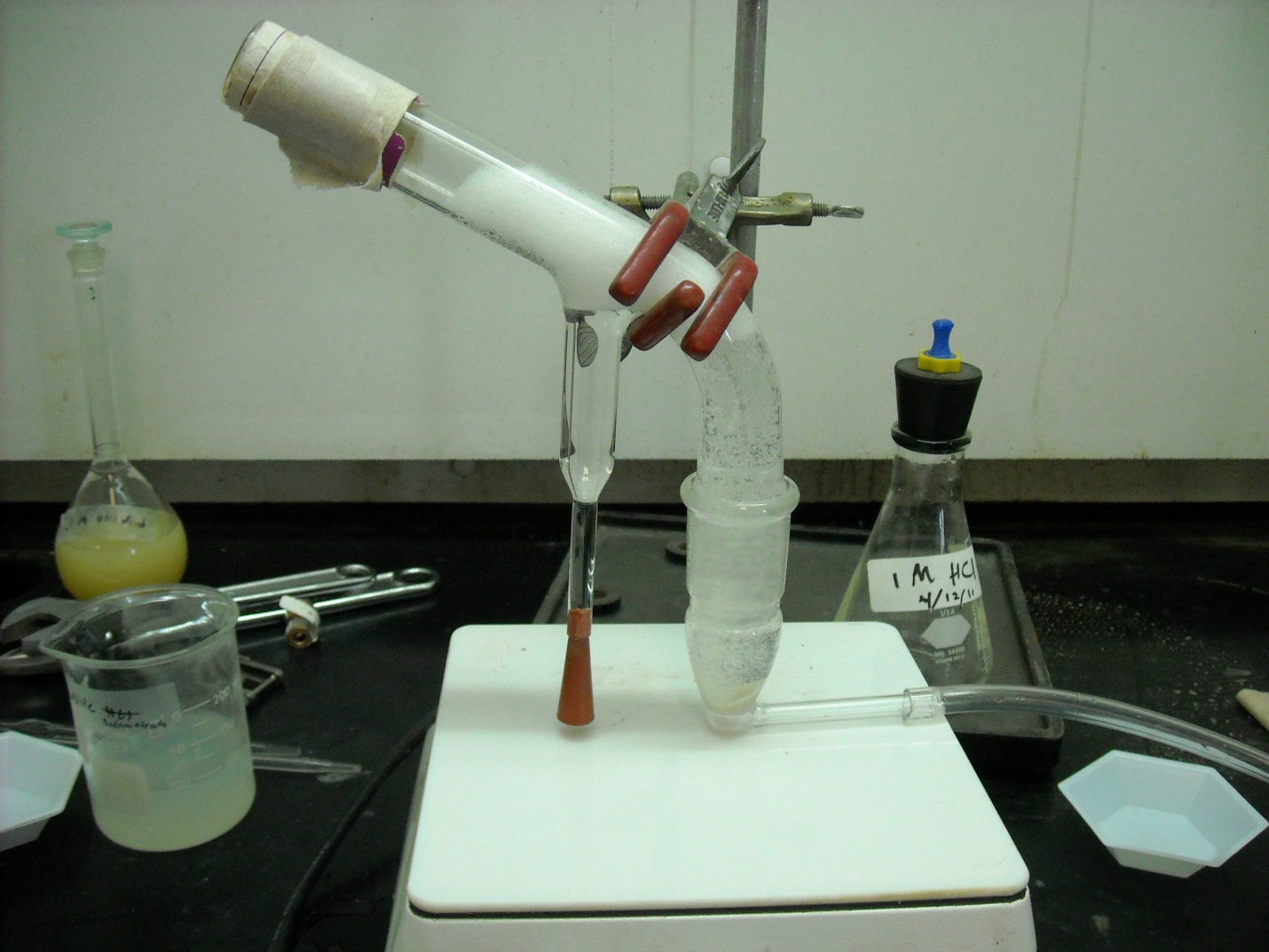
Some of the spodumene samples were crushed and ground by hand using a mortar and pestle (Figure 4). This was done in a fume hood with lung, eye and ear protection. The crushed sample was sieved using a -48+100 sieve nest and shaken by hand to separate the different sized particles. The sample pieces that were too large to fall through the 48 mesh sieve were ground again with the mortar and pestle until they were small enough to filter through. This process was repeated until about 100 grams of spodumene particles between 388 and 177 microns were obtained (Figure 4). Mineral particles of this size were recommended for Hallimond tube flotation (Feasby, 1966)



Figure 4: Grinding of spodumene (left), final spodumene particles after sieving (right)

* + 1. **Flotation**

The Hallimond tube flotation cell was set up above a stir plate and connected to a nitrogen tank (Figure 5). One gram of the ground up spodumene was placed into the cell along with a magnetic stir bar and a sodium oleate solution at a specific concentration with a pH of 9. The different concentrations used were 0 M, 0.0001 M, 0.00015 M, 0.001 M, 0.002 M, 0.003 M, 0.004 M, and 0.005 M sodium oleate. The cell was prepped for about two minutes before beginning flotation. The stir plate was turned to 700 rps while the nitrogen flowed through the system at approximately 0.75 cc/sec for 8 minutes. Any froth that overflowed from the cell was collected in a beaker and combined with other floated material. The tailings and floating were collected separately and placed on watch glasses. To speed up the drying process, these watch glasses were heated under an Ohaus Oven for at least ten minutes, depending on the wetness of the sample. The concentrate and tailings from each trial were weighed separately and the recovery was calculated using the total sample collected.



Nitrogen inlet

Initial sample location, tailings collection

Potential overflow of foam

Concentrate stem

Figure 5: Hallimond tube flotation cell with flotation in progress

1. **Results**

Several kilograms of spodumene were collected from some of the mines near Keystone, South Dakota and several kilograms manganese-bearing nodules were collected from alongside the highway near Oacoma along the Missouri River.

**4.1 X-Ray Diffraction**

X-ray diffraction (XRD) was used to analyze the spodumene samples in order to determine if the samples were essentially all spodumene or if there were other impurities in the mineral. The XRD spectrum was compared to a reference spodumene spectrum from the Black Hills (Figure 6). XRD demonstrated a strong correlation between the spodumene samples collected and reference spodumene spectrum. This indicated the sample is essentially pure spodumene.

Figure 6: Experimental spodumene sample (blue) compared to a reference spodumene spectrum (red)

**4.2 Flotation and Contact Angle**

Table 1 contains the data collected and calculated from the flotation trials. The contact angle was not taken for the first two trials because the pH was recorded to be 8 while the desired pH for flotation was 9. Thus the first two trials were discarded. Figure 7 compares percent recovery and contact angle with regards to surfactant concentration from trials 3 to 13.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Sample Trial Number | Concentration of Sodium Oleate (mol/L) | Contact Angle  (°) | pH | Notes | Recovery (%) | Percent Spodumene lost in processing |
| 1 | 0.001 M | - | 8 | Did not collect foam overflow | 43.1% | 17.99% |
| 2 | 0.001 M | - | 8 | Collected foam overflow | 38.4% | 7.99% |
| 3 | 0.001 M | 49.9 | 9 | Collected foam overflow | 37.5% | 7.15% |
| 4 | 0.0015 M | 46.4 | 9 | Collected foam overflow | 42.0% | 4.12% |
| 5 | 0.0050 M | 41.6 | 9 | Collected foam overflow | 15.3% | 3.05% |
| 6 | 0.0001 M | 47.6 | 9 | Collected foam overflow | 0.312% | 0.94% |
| 7 | 0.0005 M | 64.9 | 9 | Collected foam overflow | 15.85 | 3.33% |
| 8 | 0.0000 M | 58.4 | 9 | Collected foam overflow | 0.071% | 0.74% |
| 9 | 0.0030 M | 40.1 | 9 | Collected foam overflow | 32.6% | 1.73% |
| 10 | 0.0040 M | 42.4 | 9 | Collected foam overflow | 34.4% | 2.98% |
| 11 | 0.0020 M | 51.0 | 9 | Collected foam overflow | 37.6% | 1.33% |
| 12 | 0.0010 M | 49.9 | 9 | Collected foam overflow | 49.0% | 2.70% |
| 13 | 0.0010 M | 49.9 | 9 | Collected foam overflow | 39.1% | 1.61% |

Table 1: Results of Hallimond tube flotation trials

Figure 7: Flotation of spodumene samples and contact angles with different concentrations of sodium oleate solutions at pH 9

The standard deviation of the recovery was calculated from the three flotation trials that were run at 0.001M sodium oleate. This deviation was 6.2 percent recovery with a 95% confidence interval of 7.0 percent recovery. When this deviation is added to the graph, it shows that the percent recovery of spodumene from the trials between 0.001 and 0.004 M sodium oleate are statistically equivalent. Thus the significance of their differences is questionable (see figure 8).

Figure 8: Flotation of spodumene samples and contact angles with different concentrations of sodium oleate solutions at pH 9 including the standard deviation of percent recovery.

1. **Discussion**

Due to time constraints and the desire to conduct new research, spodumene became the focus of this project. Thus, the contact angle and the flotation separation process were not conducted on the manganese samples.

Obtaining consistent results with the contact angle goniometer was very difficult. The drop size was altered several times until a good volume was found that was not too large for the camera to record the entire drop but not too small as to not have a difference in advancing and receding angles. Even with a consistent volume of 10µL per drop, placing the liquid in one location on the sample without accidentally spreading the drop with the dropper rarely happened. Thus a lot of data was thrown out due to morphed droplets. Another inconsistency was the sample surface itself. The surface was polished but some smaller craters and cracks still existed on the surface which morphed the droplet. After the droplet was successfully placed, it naturally began to spread out and evaporate which then lowered the contact angle. To avoid this issue, the contact angle was measured as quickly as possible once the droplet was placed. This may explain why, at extreme high and extreme low concentrations of sodium oleate, the contact angles were unexpectedly high. The contact angle could have been measured prematurely before a more realistic equilibrium with the droplet on the surface could be reached. Because of all these factors, the contact angles obtained may not be as accurate as desired.

When the contact angles were first calculated, the angles were so variable that the surface was deemed to have too much inconsistency. After taking a closer look at the surface under a microscope, it was discovered that the polishing component was not completely removed from the surface and so was distributed all over the spodumene. After further cleaning with nylon brushes, the surface no longer had visible polishing component and the contact angles were more consistent.

F:\REU SDSMT\Microscope\X1000 Spodumene2.tifF:\REU SDSMT\Microscope\X1000 Spodumene1.tif

Figure 6: Polished spodumene sample before cleaning with a nylon brush (left) and after (right)

When collecting the separated spodumene after performing flotation, the tailings were easier to collect than the floatings. The tailings remained in one location on the bottom of the Halllimond tube cell, so was easily scooped onto the watch glass for measurement. The concentrate, however, were not only in the concentrate stem, but also in an overflow beaker and stuck along all the inside of the flotation glassware. Thus, the recovery is likely to be lower than the actual amount of spodumene that floated due to loss from the collecting process.

As more trials were performed, the percent of spodumene lost from the initial amount used decreased, most likely due to the increased skills of the experimenter. Because of this, the standard deviation may not be as accurate as it could be because the data gathered to calculate the standard deviation came from one of the first trials and two of the last trials.

1. **Conclusion**

X-ray diffraction demonstrated that the samples were essentially pure spodumene. Because of this, then the percent recovery is sufficient to analyze how successful each flotation trial floats spodumene rather than analyze specifically what floated and what remained in the tailings.

From concentrations of 0.001 to 0.004 M there is a consistent correlation between the percent recovery of spodumene and the contact angle of spodumene. With a higher contact angle, the percent recovery tended to increase as well. More data is necessary to conclude the significance of the concentration of surfactant with the contact angle differences and percent recovery.

However, at the extreme ends of the concentrations of flotation (from 0 M to 0.001 M sodium oleate and 0.005 M sodium oleate), the recovery significantly declined, while the contact angle remained relatively high. The extreme low and high concentration contact angles were unexpected because in general high contact angles mean the sample has high hydrophobicity, and thus, would be more likely to attach onto the nitrogen bubbles in flotation. These results could be due to surface roughness or precipitation of metal oleate species at the mineral surface. There is also a high chance that the contact angles were measured prematurely before the droplets fully expanded to their proper contact angles.

1. **Future Work**

For future work, several variables regarding the Hallimond tube flotation can be changed. This project only had ten useful flotation trials, but more trials of different concentrations will help determine the significance of the changes in percent recovery and contact angle in relation to sodium oleate concentration. The pH of the system can be adjusted to a pH higher or lower than 9 in order to see how significant the pH affects the flotation recovery and contact angle. The time chosen to run a flotation can be increased to determine the most effective time in terms of percentage of floatings recovered. Finally, the particle size of the spodumene can be altered to determine the optimal particles size that is best for flotation.

More data on the contact angle of spodumene at different concentrations of sodium oleate is necessary to get a more accurate idea of the true contact angle. The contact angle can also be measured with a focus on how it changes as a function of time in order to reduce prematurely measuring the contact angle before the droplet fully spreads on the sample surface.

Finally, large scale froth flotation can be run on the samples to go beyond Hallimond tube flotation. This would be more applicable for industry to try large scale flotation and find out if the recovery is better or worse than small scale Hallimond tube flotation.

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