

**SEPARATION OF NMC AND CARBON NANOPARTICLES  
VIA SEDIMENTATION FOR LITHIUM-ION BATTERY  
DIRECT RECYCLING**

by

Stephanie N. Ross

A thesis submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Honors Degree in Mechanical Engineering with Distinction

Spring 2022

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## ACKNOWLEDGMENTS

I would like to thank my Thesis Director, Dr. Koffi Pierre Yao, for supporting and funding this study. Dr. Yao took a gamble in allowing me to perform this work in his laboratory, despite the capital needed to conduct battery recycling research not being present at the time. Nonetheless, he helped me obtain the sometimes-unorthodox equipment I required for my experiments and served as a knowledgeable resource to consult regarding experimental design, data analysis, and communication.

I also acknowledge my second and third readers, Dr. Ajay K. Prasad and Dr. X. Lucas Lu. Both professors have given me valuable feedback, questions, and advice. Dr. Prasad has served as a long-time mentor throughout my education at the University of Delaware. Over the years, he has provided invaluable advice in navigating the world of academia and encouraged me to pursue my research and professional goals.

I am grateful for the assistance of Whitney Sample, Scott Nelson, and Chin Chen Kuo. Mr. Sample provided design suggestions for the development of the acrylic tube holder and divider, and he laser cut the designed pieces in his facilities. Mr. Nelson cut a stainless-steel component in his machine shop so that it would fit inside the sedimentation pool. Mr. Kuo trained me to perform TGA and assisted me as I characterized my samples.

I thank my family and friends—especially my mother and father—for always cheering me on. They are my role models and provided ample support throughout this study.

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## **ABSTRACT**

Lithium-ion batteries are used in a variety of electronics today and are expected to increase in usage with the rise in electric vehicles. However, the recycling processes of these batteries must be improved to reduce or eliminate the environmental harm created by them. This thesis features the separation of cathode active material in water through the use of a sedimentation pool. The settling behavior of NMC and carbon nanoparticles is characterized by a set of graduated cylinder experiments, where it was found that carbon nanoparticles will typically float in water if they do not form large agglomerates. Observations from this set of trials align with the principles of Stokes' Law and the interparticle collision theory. Operating parameters of the constructed sedimentation pool were determined through flow visualization and NMC displacement trials. In the NMC region of the sedimentation pool, 92 wt.% of the collected particles were determined to be NMC through the use of thermogravimetric analysis. In the carbon region of the pool, 60 wt.% of the sample collected was NMC. The large amount of NMC collected in the carbon region is suspected to be a result of the formation of carbon agglomerates which trap the metal oxide. The conclusion of the report discusses design recommendations.

## **Chapter 1**

### **INTRODUCTION & BACKGROUND**

Batteries have become increasingly important in sustainability efforts and clean energy. The lithium-ion battery (LIB) is currently used in applications ranging from toothbrushes and watches, to cellular phones and even automobiles. LIBs have become the standard for rechargeable energy sources due to their high energy density, ability to deliver high voltages, low-maintenance, and low tendency to self-discharge<sup>[1]</sup>. Unfortunately, these batteries continue to have notable issues and areas for improvement. Many efforts have been and continue to be made to increase the energy density, lessen the environmental impact, reduce production cost, and boost the safety of them. However, one area only recently being studied with the same degree of attention is the recycling of these energy devices at end-of-life.

#### **1.1 Research Scope**

The work conducted throughout this study was completed with the goal to develop a system for the separation of LIB active electrode materials without chemical additives. Such a system would have the potential to separate compounds in battery “black mass” after active film delamination from the foil substrate and binder removal processes. Therefore, a sedimentation pool was developed and used for the separation of cathode compounds based upon their unique material properties.

## **1.2 LIB Cathode Compositions**

LIB cathodes are typically composed of three core materials: a lithium metal oxide, conductive carbon black, and an inert binder. The binder is usually polyvinylidene fluoride (PVDF), which has good electrochemical stability in cell conditions. The binder holds the metal oxide and carbon black in a network that forms the active material film, which is then laminated on aluminum substrate to create the finished cathode electrode. More variation is typically found in the metal oxide and carbon black chosen. A commonly used and researched metal oxide is lithium nickel manganese cobalt oxide (NMC). This family of metal oxides is known for operating at high potential with high specific energy, power, and currents<sup>[2]</sup>. This makes them ideal for electric vehicles, where the goal is to have the car travel a long distance with each charge.

## **1.3 Industrial Recycling of LIBs**

Currently, most LIBs are discarded when they are no longer usable, despite their recyclability and precious chemical compositions. Reasons for the lack of recycling include the high cost and complexity of the recycling process, which typically involves smelting: using heat to melt and extract metals from other compounds<sup>[3]</sup>. Recycling could reduce the need to mine for new sources of lithium and other critical resources such as cobalt and nickel. Excessively mining a nonrenewable resource presents a sustainability challenge in itself, but mining also releases sulfur-containing compounds into the atmosphere at a significantly greater extent than smelting. Another traditional recycling method involves using strong organic solvents to dissolve compounds that are not of interest, which creates a problem of what to do with the resulting toxic waste.

## 1.4 Direct Recycling Efforts

Thus, there is a need to make the recycling process for LIBs greener. Several startups and research institutions have made efforts in LIB direct recycling, which preserves the material properties of used compounds during the recycling process. Groups are looking for ways to recover lithium and metal oxides from the cathodes using heat, mechanical forces, and less hazardous solvents<sup>[4]</sup>. One area of interest is the use of froth flotation, which separates a mixture of active materials based upon wettability. Using chemical additives in a flotation cell to generate a froth allows for hydrophobic materials to rise to the surface of the water while hydrophilic materials stay in the pool and are eventually collected in the tailings. Lei Pan and Tinu Folayan of Michigan Technological University<sup>[4]</sup> demonstrated the use of froth flotation to separate a mixture of lithium nickel cobalt aluminum oxide (NCA) and lithium manganese oxide (LMO), with over 90% recovery of NCA in the froth.

Other groups have investigated the delamination of cathode active material films from aluminum substrate. This is accomplished by targeting the binder, which adheres the film to the foil during lamination. Ethylene glycol (EG) has been found to delaminate the film in less than 10 seconds by heating the solvent anywhere from 160 to 198°C<sup>[5]</sup>. In addition, the use of dimethylsulfoxide (DMSO) has been observed to dissolve PVDF to form a slurry of active material during electrode fabrication<sup>[6]</sup>. The same method could therefore be used to dissolve the binder in a film intended for recycling. By combining these two processes, a mixture of just NMC and carbon black should be obtained. As such, the study outlined in this thesis utilizes a mixture of NMC and carbon black to separate in a water-based method similar to the work performed by Pan and Folayan. The goal is to simplify water-based separation both in equipment needed and the elimination of chemical additives.

## 1.5 Principles of Sedimentation and Separation

Sedimentation features solid particles descending in a column of fluid. The rate at which particles settle is dependent on several properties of the particles (density, size, etc.) and the fluid (viscosity, density, etc.). Because of this, it is possible to separate different solid particles using sedimentation. This study will feature the separation of NMC and carbon black in a simple, water-filled sedimentation pool.

There are many environmental parameters that affect the settling behavior of particles in a liquid. Both liquid and solid particle characteristics play a role. Namely, the settling velocity of a solid particle in a suspending fluid is a function of the density and viscosity of the fluid, as well as the density and diameter of the particle. For dilute solutions<sup>[7]</sup>, Stokes' Law gives the settling velocity of spherical particles as:

$$V_{Stokes} = \frac{g(\rho_s - \rho_f)d^2}{18\mu} \quad (1.1)$$

As such, it would be expected that increasing the viscosity of the fluid would directly decrease the settling velocity. Denser particles will settle faster than lighter particles in the same fluid. In addition, larger particles would settle faster than smaller particles of the same composition. The latter observation is particularly important when considering the phenomenon of interparticle collisions. As particles collide, the effective diameter increases, which leads to the system of particles falling faster than they would have alone. In other words, agglomerates of particles would fall faster than individual particles. Likewise, particles that are more densely packed in an otherwise dilute environment would fall more rapidly than particles that are more dispersed in a similar environment.

## **1.6 Thesis Outline**

The following sections concern the set of experiments ran throughout the duration of this study. Chapter 2 contains the methodology and data analysis for the initial graduated cylinder trials to observe particle settling behavior. Chapter 3 discusses the flow visualization experiment conducted to determine the optimal flow rate for the particle separation trials. Chapter 4 outlines the experiment used to observe the effect of the NMC concentration in the slurry feed on particle horizontal displacement in the sedimentation pool. Chapter 5 contains the final set of trials where NMC and carbon black were separated. Lastly, Chapter 6 serves as a conclusion and includes recommendations for future research.

## Chapter 2

### GRADUATED CYLINDER SEDIMENTATION

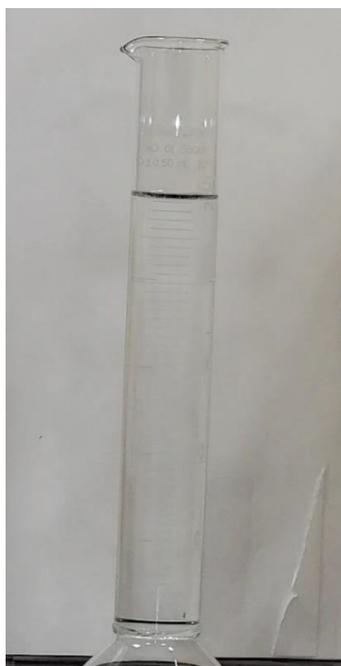
Prior to the development of the sedimentation pool, the behavior of NMC and carbon black particles needed to be described. Ideally, the two compounds would have significantly different settling patterns based upon their differences in density and hydrophilicity. NMC is over twice as dense as carbon. In addition, NMC is relatively hydrophilic compared to the superhydrophobic carbon black<sup>[8]</sup>. As such, it would be expected that NMC particles would settle more readily than carbon nanoparticles. The trials outlined in this chapter were conducted to test this theory. Water, IPA, and DMSO were used to determine how the viscosity and density of the liquid affected the settling behavior of the particles.

**Table 2.1:** Material properties of used substances<sup>[9][10][11]</sup>.

Material	Density, $\rho$ [g/cm <sup>3</sup> ]	Viscosity, $\mu$ [cP]	Surface Tension, $\sigma$ [dyn/cm]
NMC 622	4.60	--	--
Super P Carbon Black	2 (bulk) 1.6 (powder)	--	--
Water	0.997	1.00	72.80
IPA	0.785	2.40	21.79
DMSO	1.10	2.24	43.53

## 2.1 Initial Methodology with Non-Slurry Particle Delivery

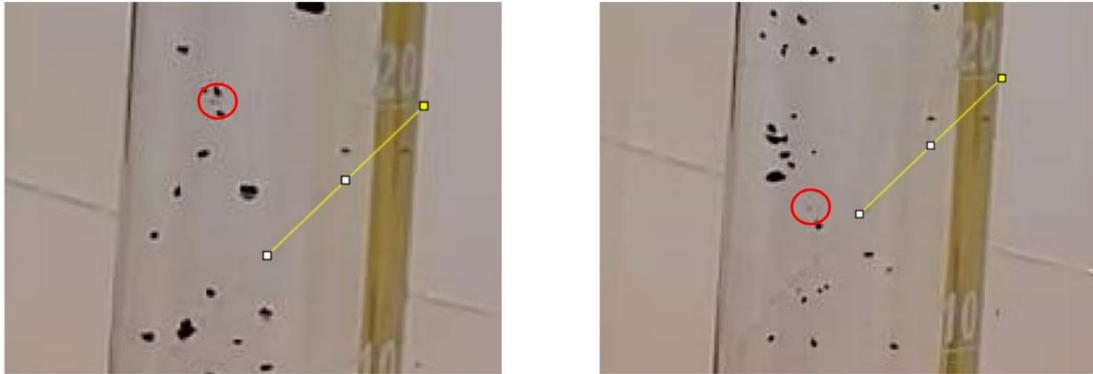
NMC and carbon particles were first gently sprinkled over the surface of either water, DMSO, or IPA in a graduated cylinder using folded weighing paper. This was performed under the assumption that particles would be ejected across the surface of the water in the final sedimentation pool. Trials were conducted with only NMC, only carbon, and an 18:1 wt.% (NMC:Carbon) mixture. This ratio was determined based upon practical cathode compositions with 90 wt.% NMC and 5 wt.% carbon black.



**Figure 2.1:** Graduated cylinder experimental setup. A white background was created to allow for the black particles to be easily observed on camera.

### 2.1.1 Non-Slurry Particle Delivery Results

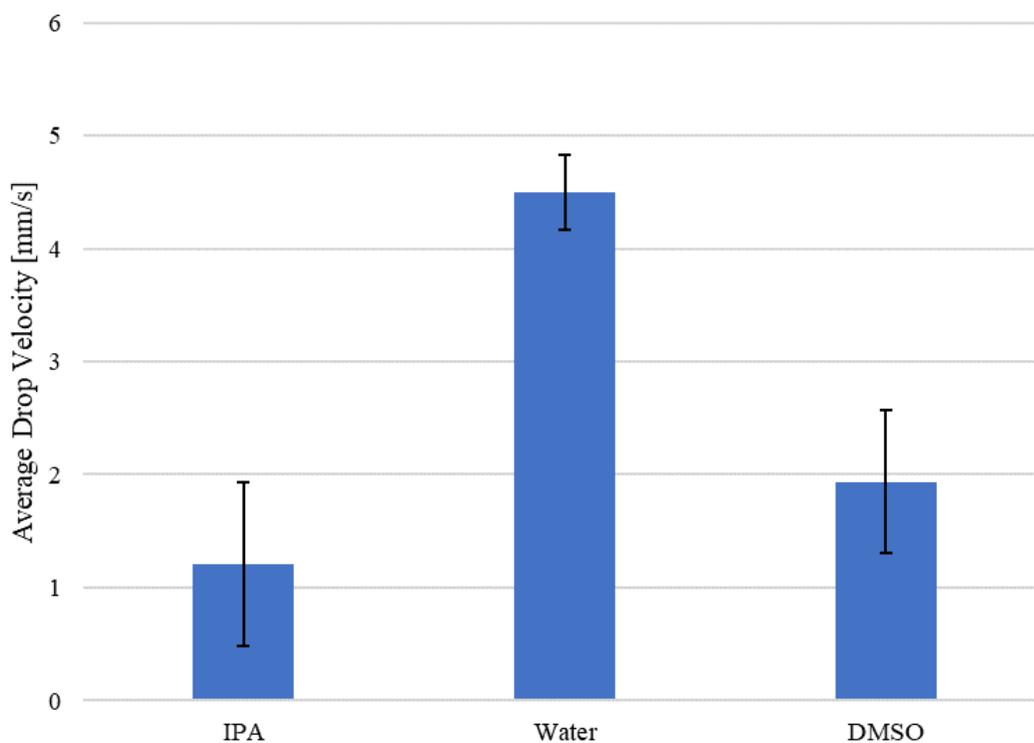
The vertical displacement of particles was recorded via video and analyzed frame-by-frame in Fiji, a derivative of ImageJ. This allowed for the drop velocity of the particles to be determined, which would give insight into how far particles might travel before settling in the sedimentation pool. A higher drop velocity indicates the particles would settle readily, corresponding to a shorter distance traveled in the horizontal direction.



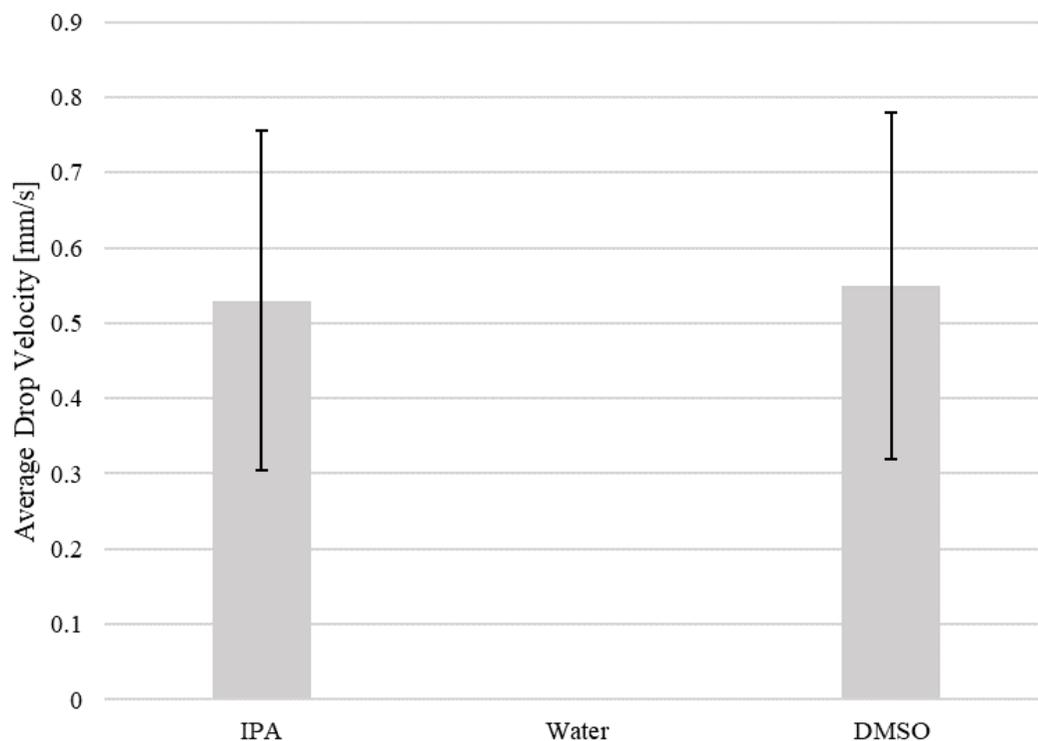
**Figure 2.2:** Carbon particle displacement tracking using Fiji video analysis.

The velocity of the particles was determined between the 20mL and 5mL markings of the cylinder, which corresponds to a distance of approximately 12.8mm. These markings were used because they were the lowest points of the fluid column where particles were still easily visible. Videos were converted to AVI files with the same frame rate as used by the camera. This conversion allowed for each frame to be assigned a particular timestamp. To determine the velocity of the particles, the timestamp of the frame where particles were at the 20mL marking was subtracted from the timestamp of the frame where the particles were at the 5mL marking. Time

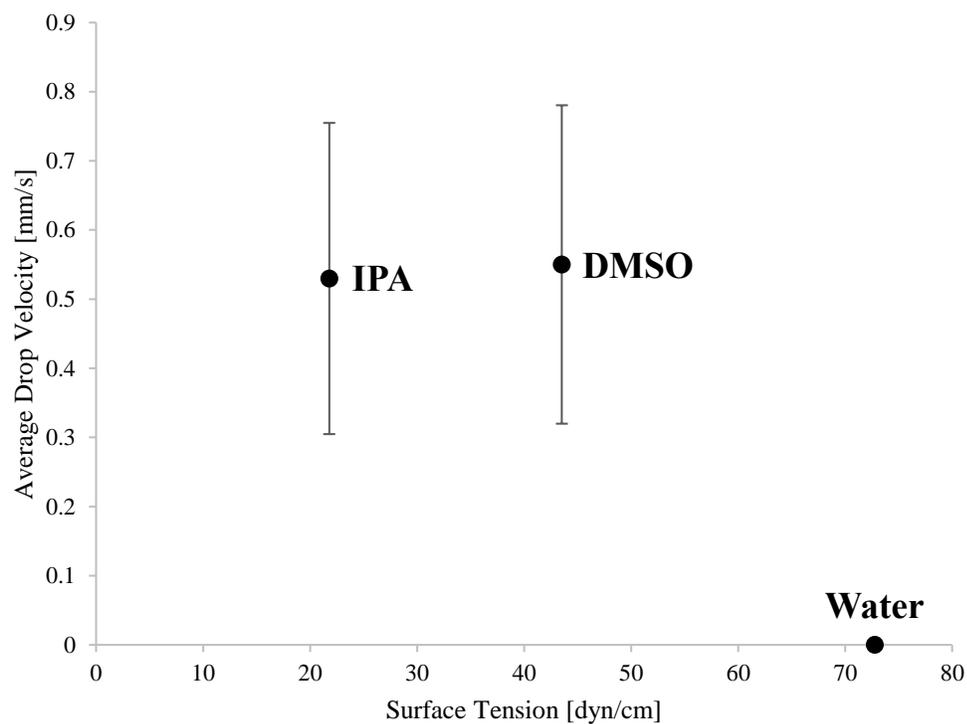
was measured in seconds, producing velocities with units of mm/s. This time-displacement data allowed for simple velocity calculations that would provide valuable information about how particles may settle in the sedimentation pool.



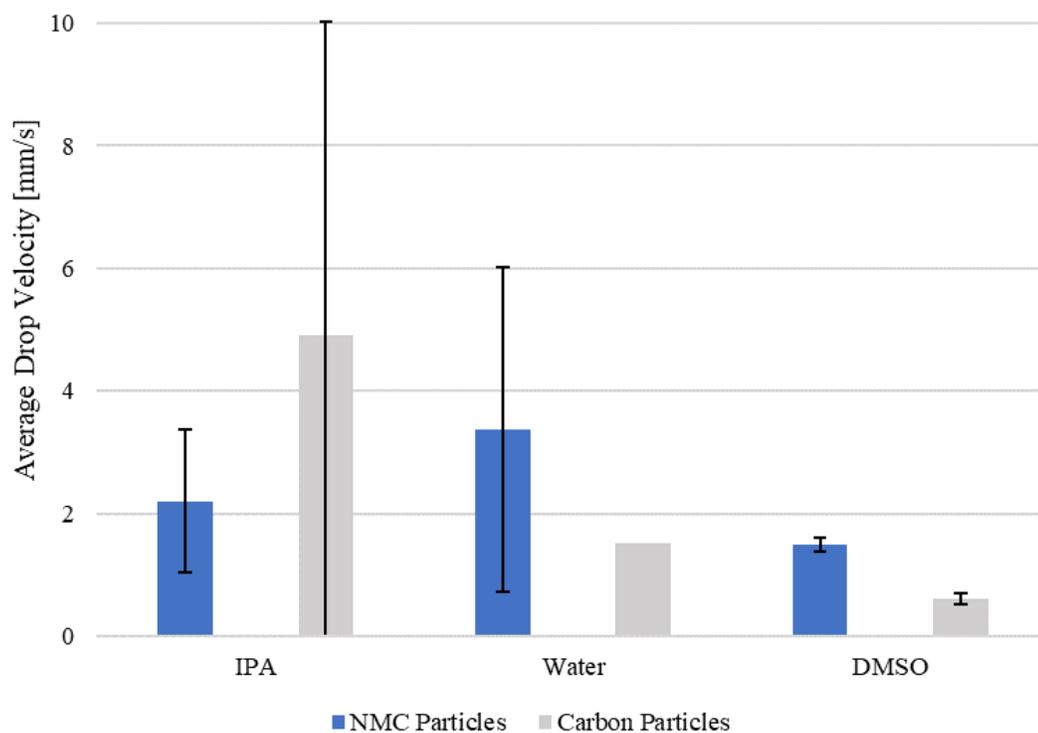
**Figure 2.3:** NMC particle drop velocity. For this dataset, particles were sprinkled on the surface of the liquid in the graduated cylinder. Initial trials with dry NMC particles found the fastest drop velocity in water with an average velocity of 4.50mm/s. The average drop velocity of the particles in IPA and DMSO were 1.21mm/s and 1.94mm/s respectively. This pattern is explained in Section 1.21.



**Figure 2.4:** Carbon particle drop velocity. For this dataset, particles were sprinkled on the surface of the liquid in the graduated cylinder. It was observed that the drop velocity of carbon particles in IPA and DMSO were similar, with velocities of 0.53 mm/s and 0.55 mm/s respectively. The settling of particles was not able to be observed in water due to the superhydrophobicity of carbon nanoparticles and the high surface tension of water.



**Figure 2.5:** The effect of surface tension on carbon particle settling. Due to the small size (20-40 nm) and relatively low density of carbon particles, the surface tension of the liquid had a significant effect on particle sedimentation. As such, only larger particle agglomerates that could overcome the effect of surface tension were able to be observed settling. Because the size of the agglomerates could not be controlled, the standard deviation of drop velocities was large. The carbon particles were unable to overcome water's high surface tension.

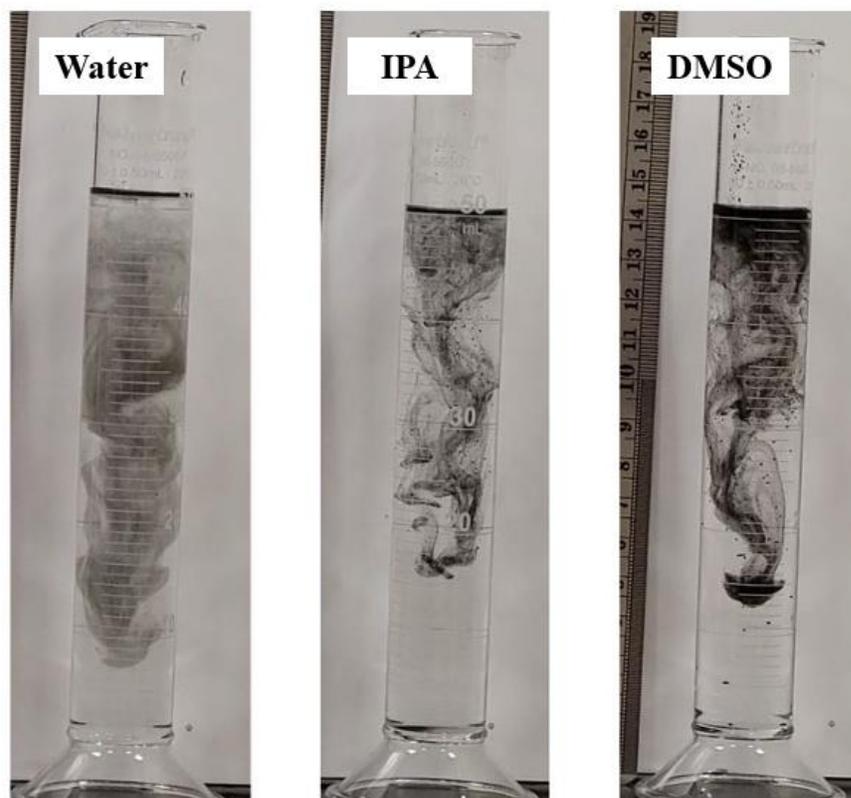


**Figure 2.6:** NMC and carbon mixture particle drop velocity. For this dataset, particles were sprinkled on the surface of the liquid in the graduated cylinder. Carbon settling in water was only observed in one trial. When using a slurry of NMC and carbon in the appropriate liquid, it was found that the presence of NMC facilitated the settling of carbon to a limited extent. Still, only the larger agglomerates of carbon were observed to settle, and the size of the agglomerates played a large role in drop velocity.

## **2.2 Slurry-Based Particle Delivery Methodology**

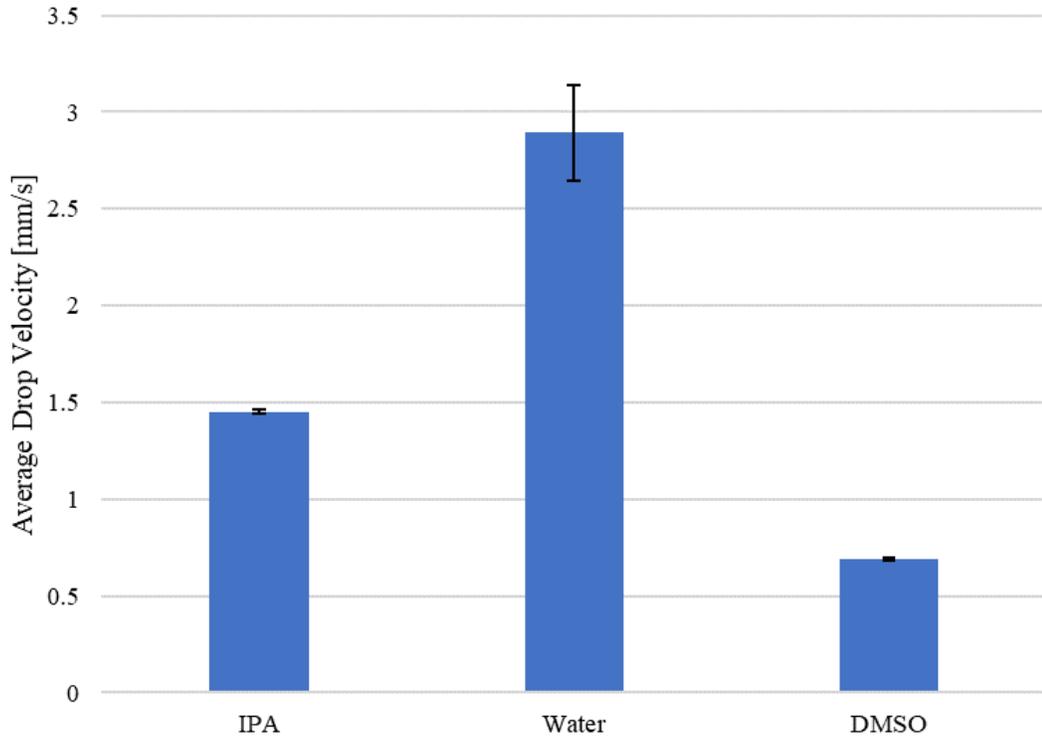
The surface tension effects of the liquids used above proved to be too large of a barrier to particle sedimentation. As such, it was determined that particles must be fed below the surface of the water in the final sedimentation pool. To prevent the formation of bubbles that would complicate the trajectory of the particles, it was also determined that the particles must be fed to the pool in a slurry. The next iteration of graduated cylinder trials was designed with this in mind.

A slurry of solid particles and the appropriate liquid was made using an ultrasonic cleaner. For each sample, 0.5g of NMC was added to 20mL of liquid, with the exception of DMSO, where 15mL of the fluid was used. A pipette was used to add the slurry to the cylinder to allow the particles to disperse themselves just below the surface of the fluid. To reduce any propulsion of the particles in the cylinder from the pipette, the slurry was delivered on the inner wall of the cylinder and allowed to slide naturally to the surface of the solvent. The freefall of the particles was recorded and analyzed using the same tracking process as before.

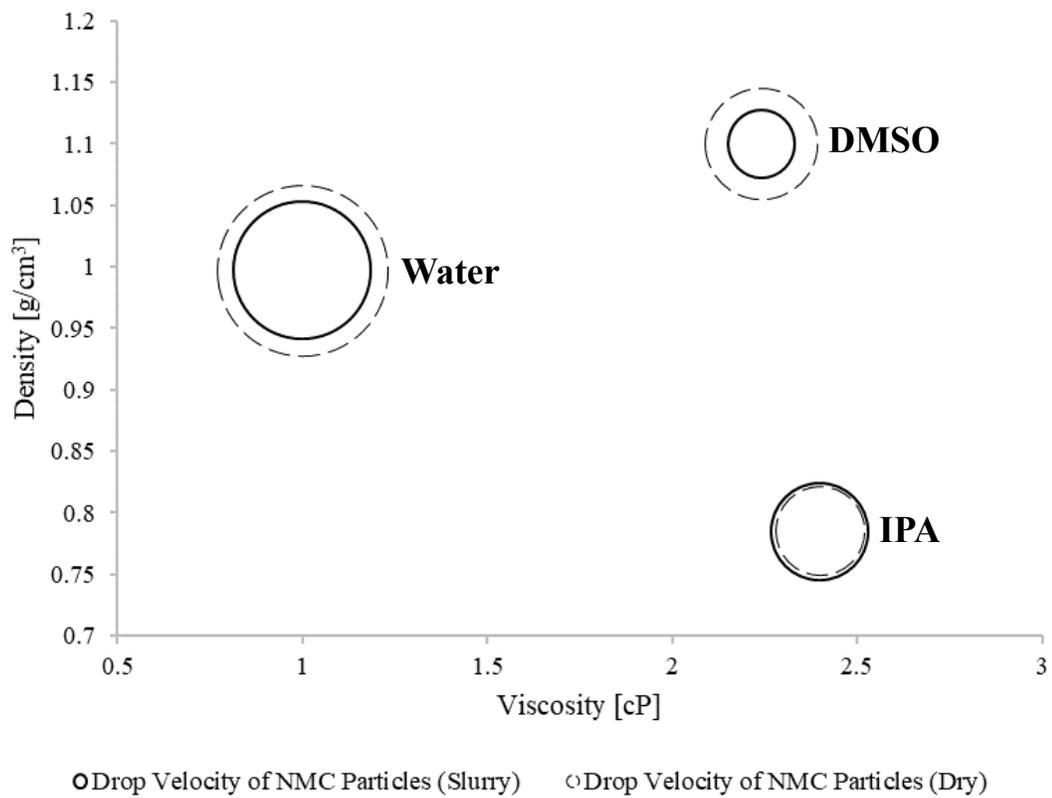


**Figure 2.7:** Mixture of NMC and carbon particles settling in water (left), IPA (center), and DMSO (right) using the slurry method. Carbon particles could be observed as independent agglomerates while NMC particles formed clouds in the fluid.

### 2.2.1 Slurry-Based Particle Delivery Results



**Figure 2.8:** NMC particle drop velocity using the slurry method in various fluids. The slurry method led to much lower standard deviations in drop velocity in the NMC-only trials. It was found that particles in water still had much faster drop velocities than those in IPA or DMSO. The drop velocity of particles in water was found to be 2.89 mm/s, while the drop velocity in IPA and DMSO was 1.45 mm/s and 0.69 mm/s respectively.



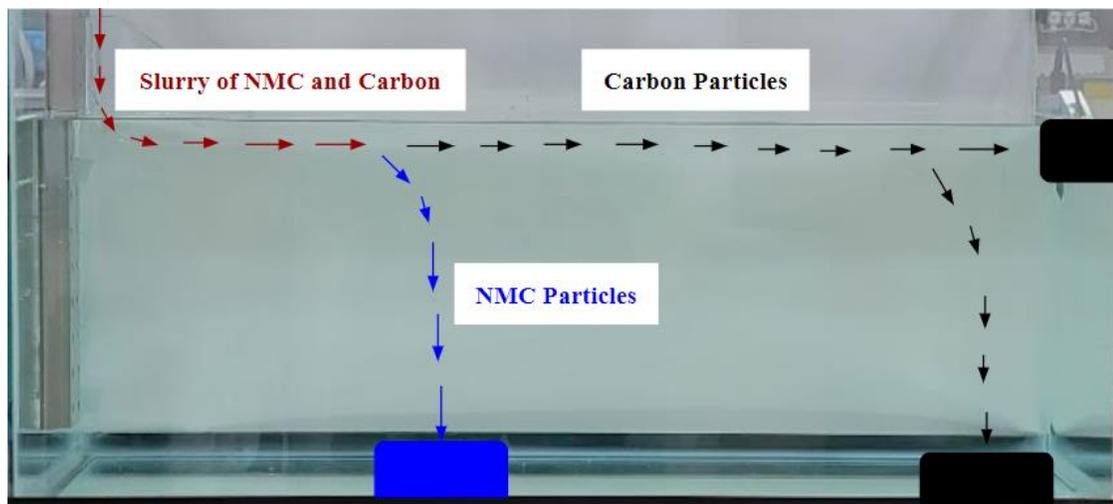
**Figure 2.9:** A visual representation of the relationship between fluid viscosity and density on NMC particle drop velocity. The magnitude of the drop velocities is represented by the areas of the bubbles. Larger bubble areas indicate a higher drop velocity.

Drop velocity in sedimentation is directly dependent on the viscosity of the fluid, as well as the buoyancy and gravitational forces experienced by the particle. NMC particles had a faster drop velocity in water than in DMSO or IPA, which is reflective of water's much lower viscosity. This trend reveals that the settling behavior of the NMC particles is primarily viscosity-driven, as expected by Stokes' Law. The difference between the drop velocity of particles in DMSO and IPA is a result of the difference in density between the fluids. DMSO and IPA are both similar in viscosity, but DMSO has a significantly higher density than IPA. As a result, the particles had a higher velocity in the IPA column than in DMSO. It could also be said that the higher concentration of NMC in the DMSO slurry could have impacted the difference in terminal velocity, however, a higher concentration would lead to a higher terminal velocity according to the interparticle collision theory. Therefore, even though the concentrations are different, the observed relationship between viscosity, density, and velocity is still scientifically valid.

Carbon settling using the slurry method was analyzed qualitatively. In general, the particles remained near the surface of the fluid even after a significant amount of time had passed. Only larger agglomerates were observed to settle slowly in water. In the NMC and carbon mixture trials, carbon partially settled in IPA and DMSO. However, the carbon particles remained on the surface of the water while NMC particles settled.

### 2.3 Graduated Cylinder Trials Key Takeaways

From these trials, it was determined that the relatively low viscosity of water would correspond to NMC particles settling quickly. This would mean that NMC should settle relatively close to the inlet of the sedimentation pool. The superhydrophobicity of the carbon nanoparticles was also confirmed by the results both in the carbon-only and NMC and carbon trials. As such, even when in a mixture, it was predicted that carbon nanoparticles would remain close to the surface of the water in the sedimentation pool or settle much farther from the inlet. Greater concentrations of NMC or larger agglomerate sizes of carbon corresponded to faster drop velocities, meaning they would land closer to the inlet of the pool. It was determined that a slurry of NMC and carbon must be fed to the pool underneath the surface of the water to overcome surface tension and facilitate repeatable particle settling behavior.



**Figure 2.10:** Expectations of particle settling behavior in the sedimentation pool.

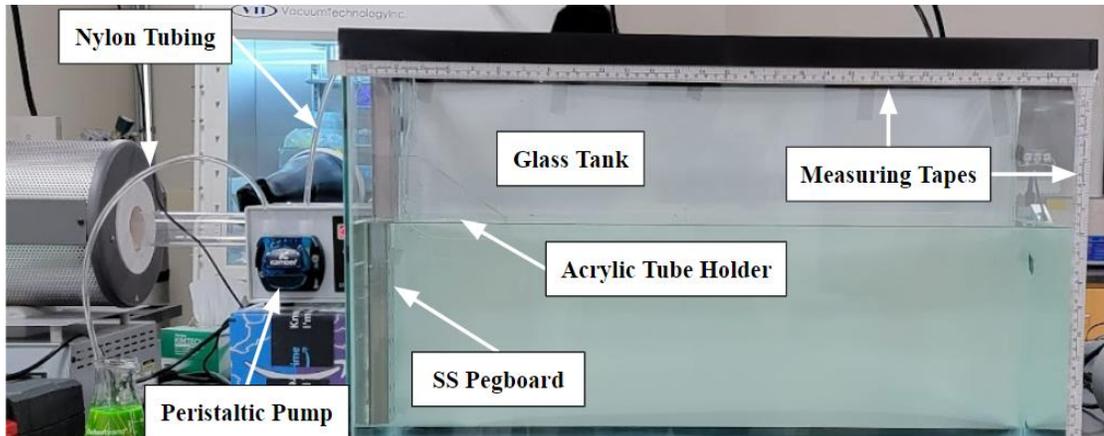
## **Chapter 3**

### **FLOW VISUALIZATION WITHIN THE SEDIMENTATION POOL**

After observing the behavior of NMC and carbon particles in the fluids, it was determined that NMC and carbon could be separated by sedimentation in water. Based upon the carbon particles' tendencies to resist settling, it was predicted that if given an initial horizontal velocity, they would maintain a horizontal trajectory for a significant duration of time. Oppositely, NMC's tendency to settle readily in water led to the expectation that particles would only travel a short distance horizontally before descending. Therefore, the experiment outlined in this chapter aimed to find an appropriate pump speed that would result in the incoming jet of water having a nearly horizontal initial profile.

#### **3.1 Development of the Sedimentation Pool**

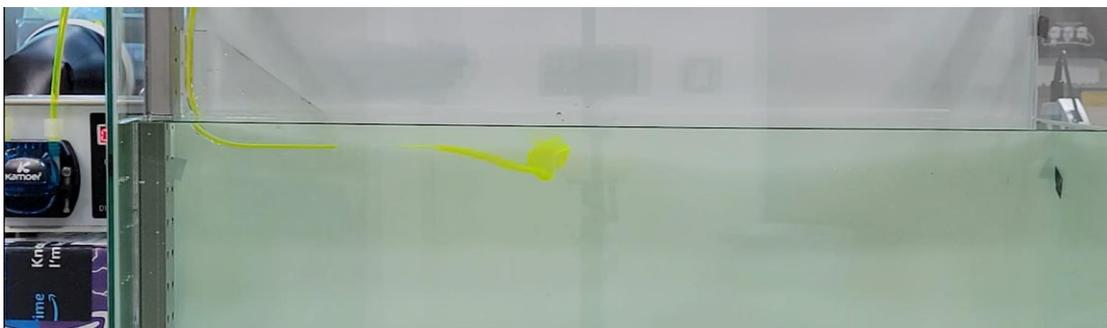
Following the graduated cylinder experiments, the sedimentation pool was designed using a commercial 29-gallon aquarium, a stainless-steel pegboard strip, and a Kamoer® DIPump550 peristaltic pump with nylon tubing. An acrylic attachment to hold the tubing horizontally underneath the surface of the water was designed and manufactured from acrylic (a complete engineering drawing of this attachment can be found in Appendix A). The pegboard was cut using a horizontal band saw in the College of Engineering Student Machine Shop, and the acrylic attachment was laser-cut in the Design Studio Fab Lab. The pegboard was adhered to one of the inner walls of the aquarium using J-B Weld Clearweld™.



**Figure 3.1:** Sedimentation pool prototype with added accessories. The accessories allowed for the depth of the water to be controlled and kept constant for each trial. Similarly, the use of the pegboard and acrylic attachment allowed for the slurry feed to be positioned at the same depth for each trial. The pump was placed on a platform so that the exit of the pump was at the same height as where the slurry would be delivered into the pool.

### 3.2 Flow Visualization Methodology

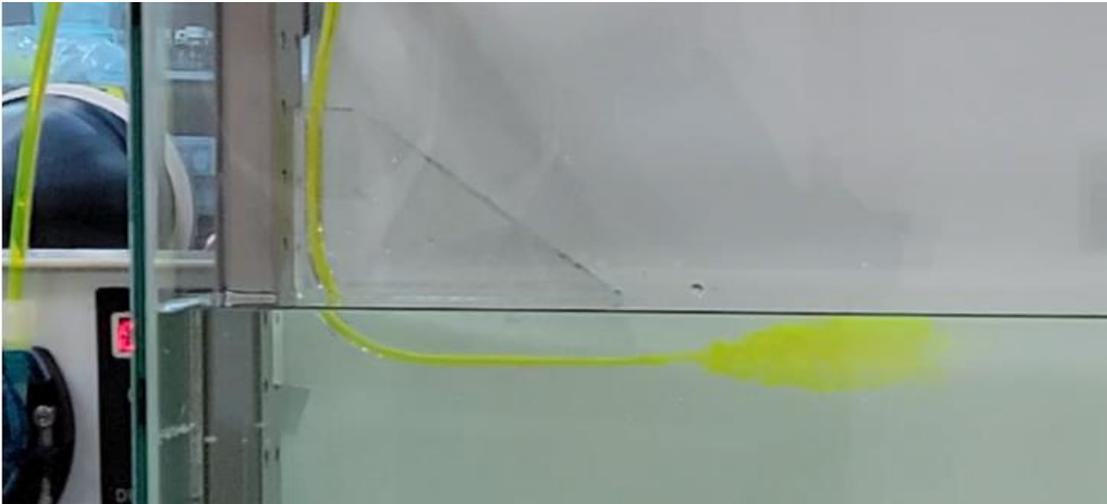
The sedimentation pool was filled with approximately 20 gallons of DI water. A solution of green tracing dye and DI water was created and fed to the pool using the peristaltic pump. Various speeds of the pump were set. The same camera from previous trials was used to record videos of the resulting flow.



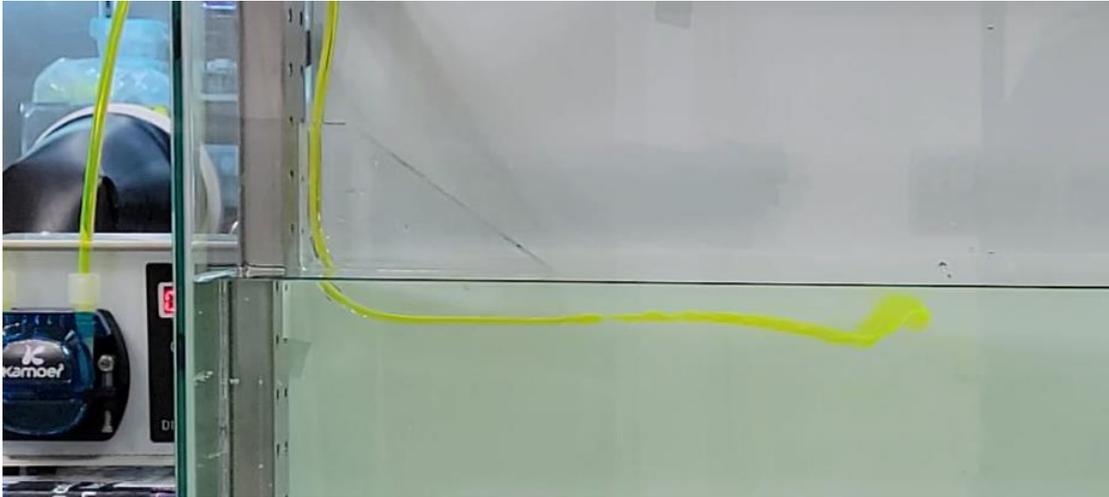
**Figure 3.2:** Tracer dye solution delivered to the sedimentation pool in a trial.

### 3.2.1 Flow Visualization Results

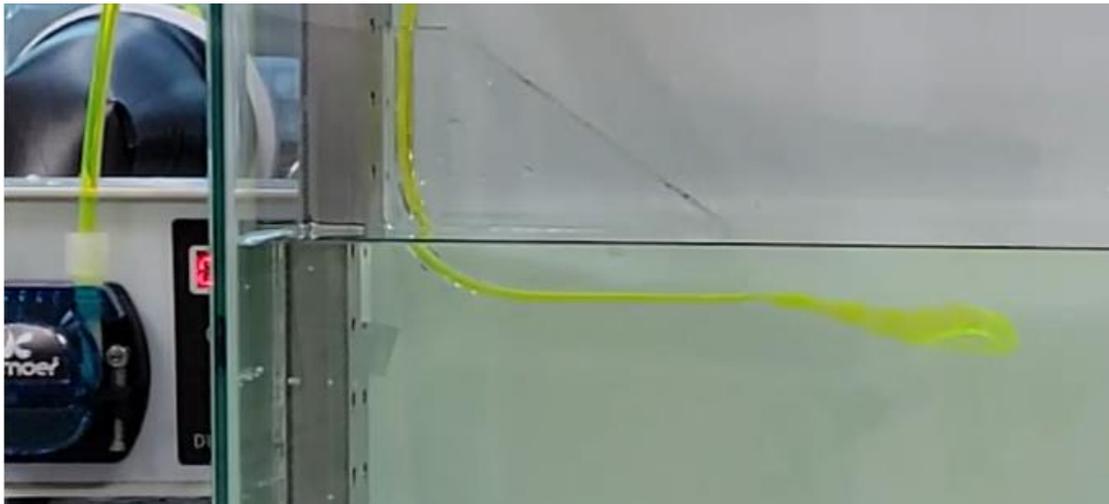
Flow rates of 55, 22, 11, and 18mL/min were tested sequentially. These flow rates correspond to settings “50”, “20”, “10”, and “15” on the pump. The following figures are snapshots of the fluid profiles of the incoming jet generated from these rates. As explained previously, the flow rate should ideally produce a horizontal initial fluid profile to allow for the separation of carbon and NMC. As such, the flow rate was reduced and increased several times to



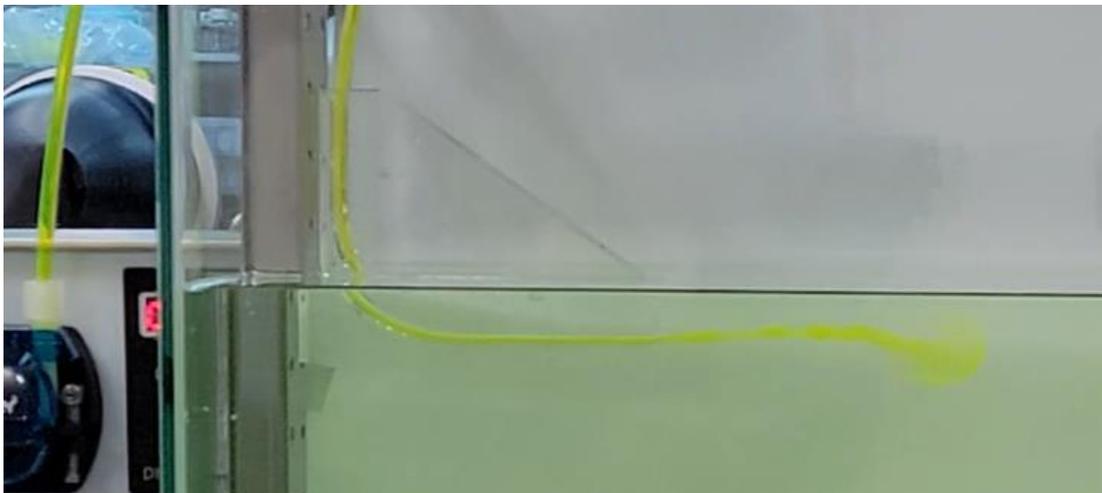
**Figure 3.3:** Fluid profile generated using 55mL/min flow rate. The initial flow generated using a 55mL/min flow rate was highly turbulent and three-dimensional. The speed was then reduced in an attempt to prevent this.



**Figure 3.4:** Fluid profile generated using 22mL/min flow rate. The initial flow generated was nearly-purely horizontal. The speed was further reduced to determine if slower flow rates would produce longer or shorter horizontal paths.



**Figure 3.5:** Fluid profile generated using 11mL/min flow rate. The initial flow generated using a 11mL/min flow rate did not produce as horizontal of a flow as the previous setting. Therefore, the speed was increased.



**Figure 3.6:** Fluid profile generated using 18mL/min flow rate. While the flow was initially horizontal, there was no perceived benefit to using the 18mL/min flow rate over the 22mL/min flow rate.

### **3.3 Flow Visualization Trials Key Takeaways**

Using either an 18 or 22mL/min flow rate resulted in horizontal initial fluid profiles. However, the rate used should be high enough to adequately drive the NMC and carbon particles through the tubing system without problem. As such, a higher pump speed was desirable to a lower one, so it was determined that the 22mL/min flow rate would be used in subsequent experimentation.

## Chapter 4

### NMC CONCENTRATION AND PARTICLE DISPLACEMENT

The final sedimentation pool would feature a divider to separate the NMC and carbon particles as they deposit. Therefore, the distance traveled by each species needed to be determined. With the assumption that carbon particles would either settle very far from the inlet of the pool or remain near the surface of the water, only NMC particles were ejected into quiescent water for this experiment. As the concentration of NMC in the slurry was found to have a large effect on the settling behavior of particle clouds, different concentrations of NMC were tested. Three concentrations were determined with the goal of finding a slurry composition that was concentrated enough to prevent NMC from traveling too far in the pool.

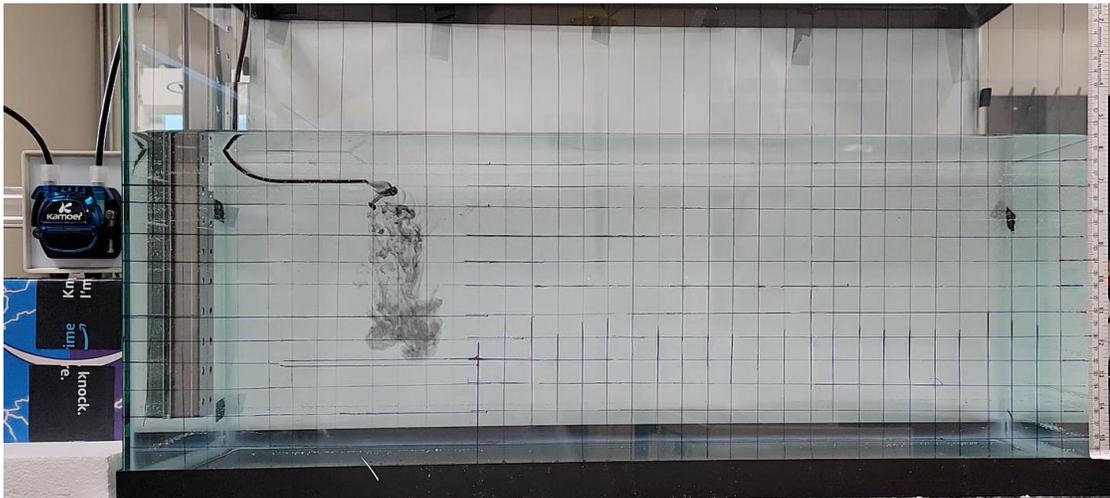
#### 4.1 NMC Displacement Methodology

A grid was drawn over the front face of the pool to allow particle horizontal displacements to be more accurately determined from video analysis. NMC particles were dispersed in vials of water through ultrasonication for one minute followed by vigorous shaking. Concentrations of NMC varied by the following amounts:

- 0.25g in 15mL of water → 0.17 M
- 0.5g in 15mL of water → 0.34 M
- 1.0g in 15mL of water → 0.68 M

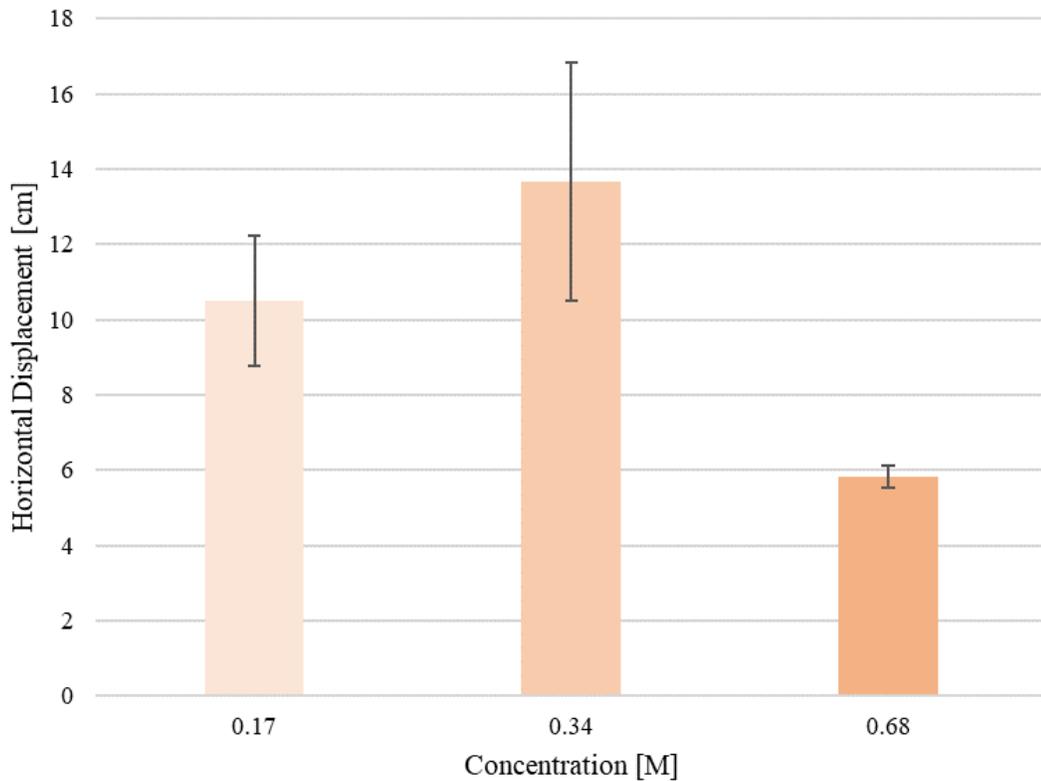
After the suspension was formed, it was fed to the pool using the peristaltic pump at a flow rate of 22mL/min. It was determined that a wall height of 16cm would

be used to not obstruct the path of carbon particles in the final system. Thus, the maximum horizontal displacement of the NMC particles at a height of 16cm from the pool floor was recorded for each concentration. Three trials were performed for each concentration.



**Figure 4.1:** NMC displacement in the sedimentation pool experimental setup.

## 4.2 NMC Displacement Results



**Figure 4.2:** Horizontal displacement of NMC particles in the sedimentation pool for different concentrations. The displacement was determined at approximately 16cm from the pool floor. For a concentration of 0.17 M, particles traveled 10.50 cm from the entrance. Particles traveled 13.67 cm in a concentration of 0.34 M. For the 0.68 M slurry, particles only traveled 5.83 cm.

### **4.3 NMC Displacement Key Takeaways**

The results of testing verified that the concentration of the slurry would need to be carefully controlled for the separation of NMC and carbon. In addition, it was learned in the original graduated cylinder trials that the presence of NMC influences the settling behavior of carbon. To ensure that the carbon particles would be able to free themselves in a matrix of NMC, a more dilute (yet still adequately concentrated) slurry was desired. As such, it was determined that the ratio of NMC to water in the 0.17 M slurry would be used in the final experiments. With this, the wall was intended to be positioned about 13cm from the inlet of the pool to ensure no NMC would cross over into the intended carbon region.

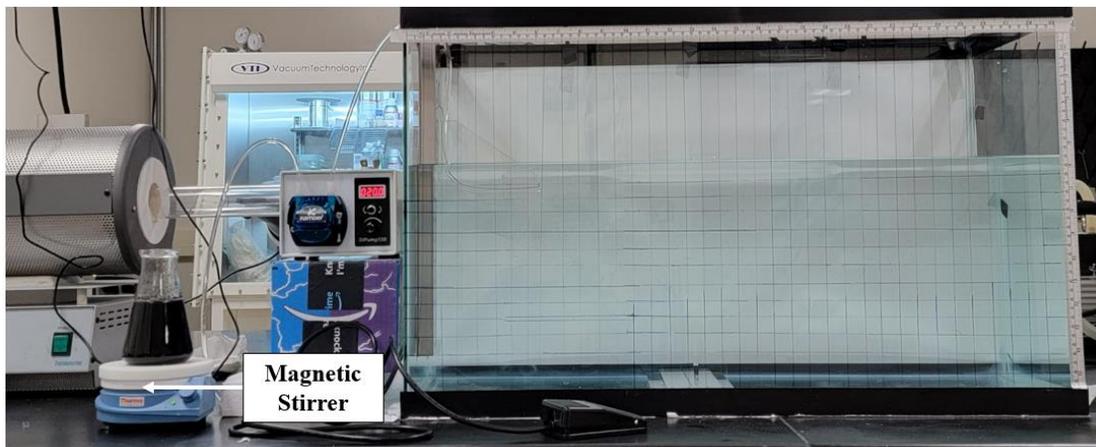
## **Chapter 5**

### **SEPARATION OF NMC AND CARBON BLACK**

The final experiment concerns the separation of NMC and carbon nanoparticles using the knowledge gained from previous experiments. The separation of the two solids was assessed both qualitatively on video and quantitatively through thermogravimetric analysis (TGA). The sedimentation pool designed was used to determine if NMC and carbon could be separated without the use of chemical additives in quiescent water, which would simplify the recycling process of LIB electrode materials.

#### **5.1 Separation of NMC and Carbon Black Methodology**

A divider was manufactured from acrylic sheets (engineering drawings can be found in Appendix B). Because a part of the acrylic tube holder broke during setup, a steel wire was used to help keep the attachment on the pegboard. The divider was placed 13cm from the inlet of the pool. A mixture of 3.60g of NMC and 0.20g of carbon black in a 220mL slurry with water was created by first sonicating the particles in a 150mL slurry for one minute and adding additional water. The slurry was continuously mixed with a magnetic stirrer at 150rpm in an Erlenmeyer flask. The angled walls of the flask helped keep the carbon particles beneath the surface of the slurry.



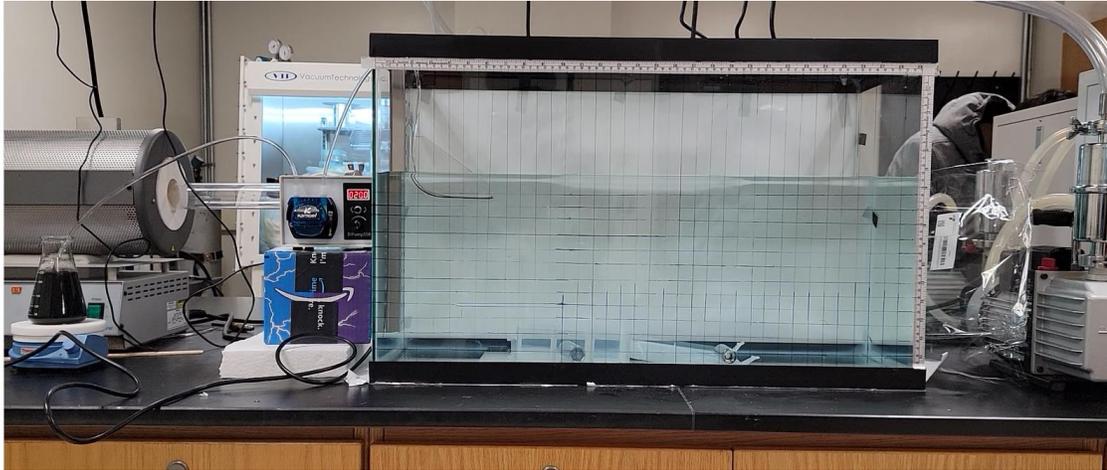
**Figure 5.1:** Sedimentation pool setup for the separation of NMC and carbon particles.

### 5.1.1 Initial Results

Upon running the first trial, it was realized that the tendency of carbon nanoparticles to form agglomerates was severely underestimated. As such, the only form of carbon that was able to successfully enter the pool were large agglomerates that fell immediately. This resulted in NMC and carbon settling on the same side of the pool floor.

### 5.2 Updated Methodology

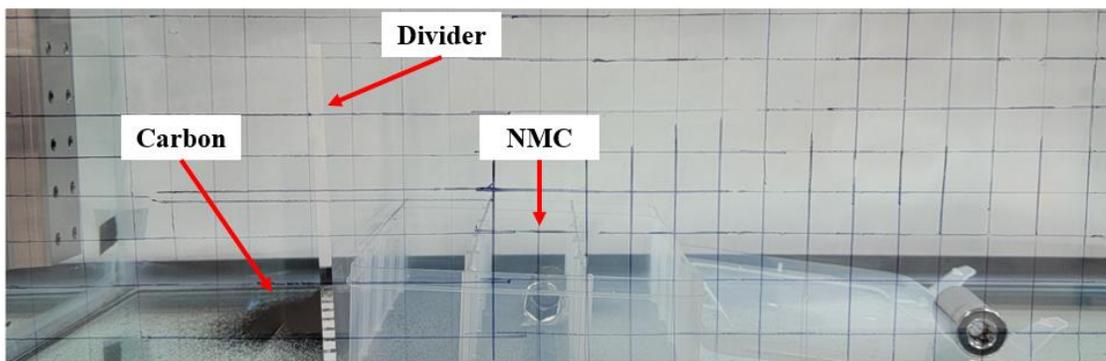
The divider was then moved to the separation point observed in the previous trial. To make the collection of NMC easier and prevent NMC from contaminating the carbon region of the pool, a plastic tray was placed on the right side of the divider. Weights were put in the tray and the lid. Two trials were then completed using the same process as before. NMC particles were collected by closing the tray and removing it from the pool, while carbon particles were collected by using a long dropper.



**Figure 5.2:** Modified sedimentation pool setup.

### 5.2.1 Separation of NMC and Carbon Black Final Results

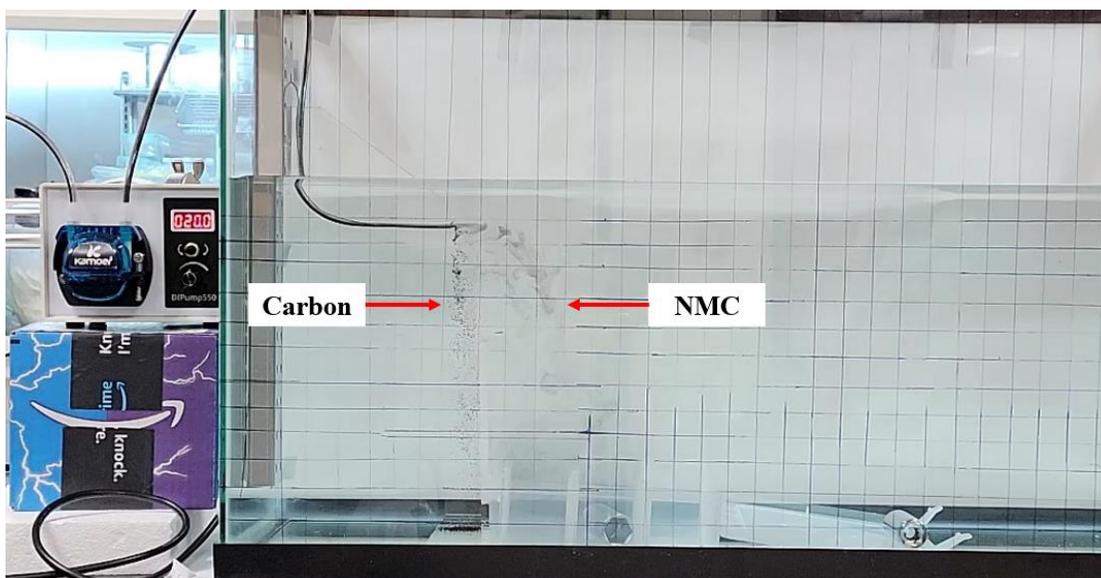
Visually, the separation of NMC and carbon particles was achieved. Some carbon agglomerates were observed to settle in the NMC tray, however, the majority deposited on the left half of the wall. In addition, some particles were found floating on the surface of the water after the system was left to rest. The bottom of the NMC tray appeared to be slightly gray, indicating that particles had indeed settled within the tray as intended.



**Figure 5.3:** Carbon and NMC deposits in the sedimentation pool.



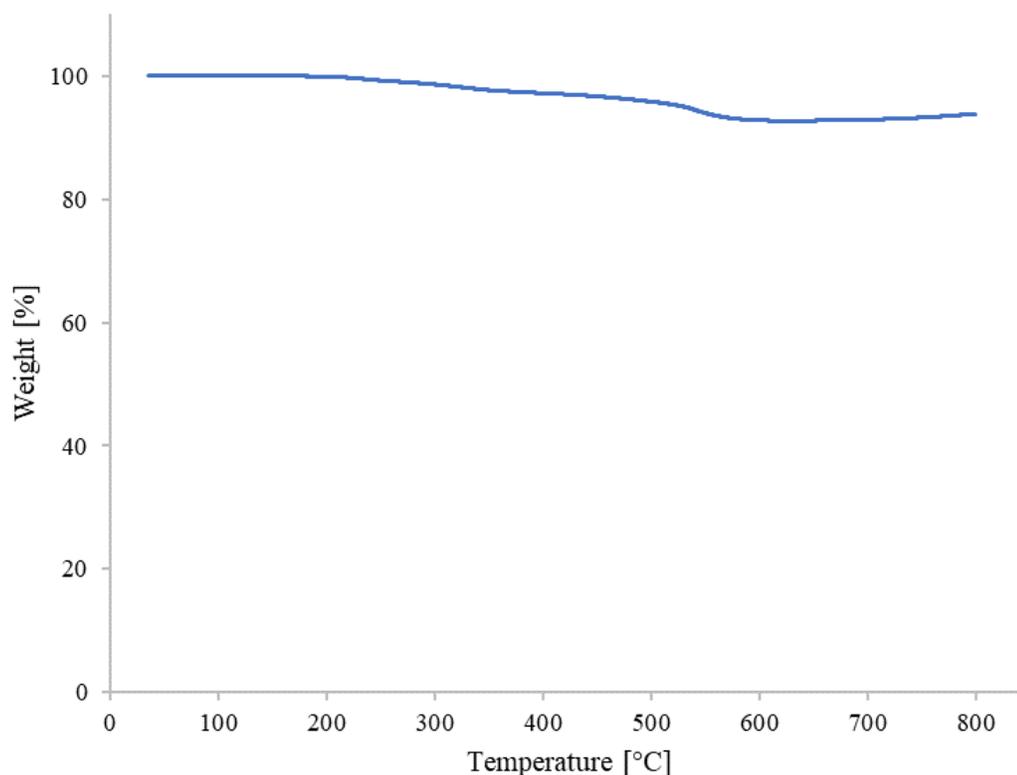
**Figure 5.4:** Particles left floating on the surface of the water.



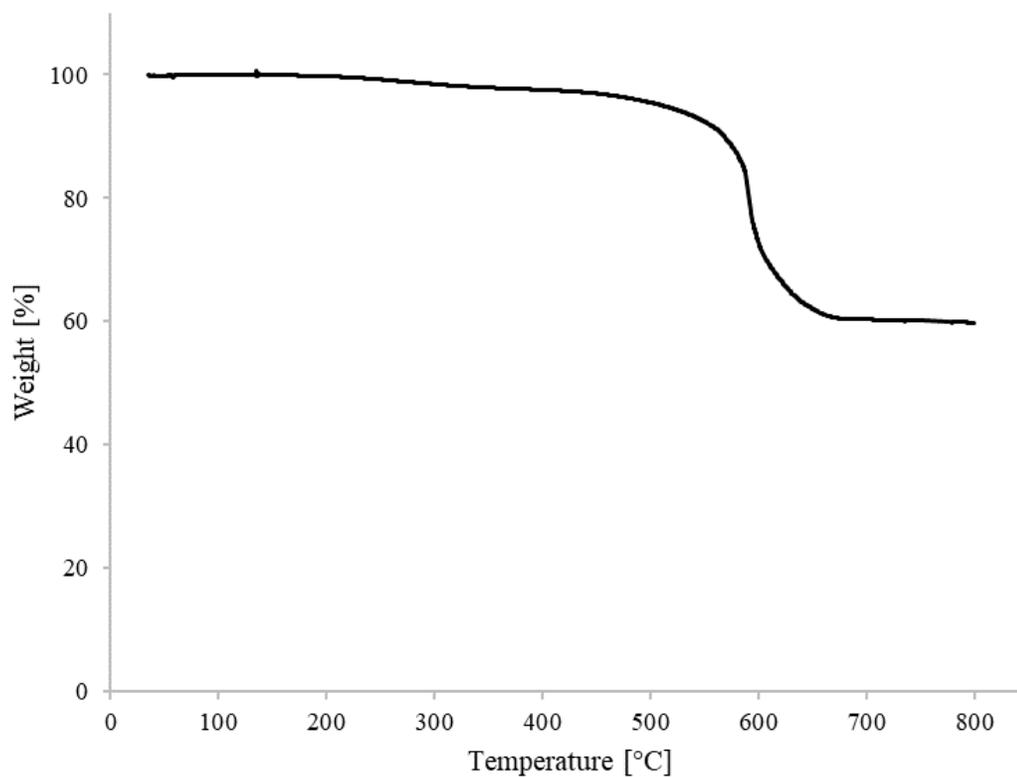
**Figure 5.5:** Separation of NMC and carbon agglomerates in the sedimentation pool.

TGA was used to quantitatively verify the separation of carbon and NMC in the sedimentation pool. Powder from each deposit was collected after allowing the particles to settle for at least 10 minutes. For the carbon deposit, particles were removed using a long dropper. Underwater, the NMC tray was closed and lifted out of the tank with the particles inside. For both types of deposits, samples were taken and water was removed with pipettes and evaporation at 70-80°C for several days. The samples were then subjected to vacuum at 100°C in preparation for TGA.

A TA Instruments® Discovery TGA system was used to analyze the particles. Samples were heated from 35°C to 800°C at a ramp rate of 20°C/min (50mL/min). The tests were conducted in an air environment to allow for carbon to gradually burn out of the sample. In this configuration, only NMC would be left in the analysis pan as residue at the conclusion of the analysis. Therefore, the changes in weight shown in the results of TGA would correspond to any carbon contained in each sample. The expectation was that samples taken from the carbon deposit would feature large reductions in weight during analysis with little-to-no residue. On the other hand, samples taken from the NMC tray should remain the same weight throughout the analysis.



**Figure 5.6:** TGA results for a sample taken from the NMC tray. After heating the sample to 800°C, only a 7.24% reduction in weight overall was achieved. There is a slight increase in weight at the end of testing, which could be due to oxidation of the metal oxide. Carbon nanoparticles have been demonstrated to burn to CO<sub>2</sub> in air at a temperature of roughly 550°C<sup>[12]</sup>. From this temperature onwards, there is a 1.29% reduction in weight. This means that likely 1.29 wt.% of the sample from the NMC tray can be attributed to carbon nanoparticles, while the other reduction in weight could have resulted from other contaminants in the sample.



**Figure 5.7:** TGA results from a sample collected from the carbon deposit. An overall reduction in weight of 40.11% was achieved. With approximately 60 wt.% left as residue at the end of the analysis, it was concluded that a significant amount of NMC had made it into the carbon region of the sedimentation pool.

### **5.3 Final Takeaways**

The results presented in this chapter demonstrate that the separation of NMC and carbon nanoparticles is possible through sedimentation. NMC fell in the sedimentation pool as dispersed clouds of fine powder, while carbon nanoparticles typically formed large agglomerates as they were driven by the peristaltic pump. The divider was placed at the point of separation between the two particle streams. While only trace amounts of carbon nanoparticles made it to the NMC region of the pool, a significant amount of NMC was found in the carbon particle deposit. Therefore, the system should be optimized in future research with the primary focus of reducing NMC particles settling with carbon agglomerates.

## **Chapter 6**

### **CONCLUSION**

The separation of NMC and carbon nanoparticles was achieved by using the sedimentation pool developed. Parameters and characteristics of the pool were determined prior to development through a series of several experiments used to characterize the settling behavior of NMC and carbon. In these experiments, the effect of numerous properties such as fluid viscosity, density, and surface tension, as well as particle density and size were observed.

Results of initial testing showed promise that NMC and carbon could be separated relatively easily in water largely due to the superhydrophobic nature of carbon nanoparticles. However, the tendency of the carbon particles to form agglomerates in water was underestimated following the graduated cylinder trials. As such, the sedimentation pool had to be adjusted to segregate the large agglomerates closer to the inlet of the prototype. While the agglomeration helped to prevent carbon from traveling a longer distance into the NMC region of the pool, significant amounts of NMC were deposited in the carbon region. This raises the possibility that carbon agglomerate formation traps NMC particles. Therefore, optimization of the particle feed into the sedimentation pool is required to minimize the trapping of NMC particles inside carbon agglomerates.

While this study provides a baseline for the separation of LIB active electrode materials using water with no chemical additives, the system developed should undergo modifications to improve the collection of settled particles. In addition,

improvements must be made to inject the slurry of particles into the pool without the formation of carbon agglomerates. The stepper-motion of the peristaltic pump proved to agitate the particles enough to promote the formation of agglomerates. As such, a pump with continuous flow should be used instead. A predictive model should be used to determine if the separation of particles would be achieved in water, where the quantity of water, concentration of the inlet slurry, and particle properties should be accounted for. The model should utilize the Stokes' equations for settling velocity and drag to determine the trajectory of particles with consideration to buoyancy and gravitational forces.

Lastly, the results of this study provide information that could prove useful to making the recycling of LIBs more environmentally-conscious. Although the separation of NMC from carbon is not necessarily a focus in today's direct recycling efforts, the partial success of separating these compounds shows that as long as the particles used vary enough in material properties, different compounds can be separated without the use of added chemicals. An optimized water-based sedimentation pool could be used to separate NMC or other lithium metal oxides from graphite in battery black mass, which is of much greater interest within the field.

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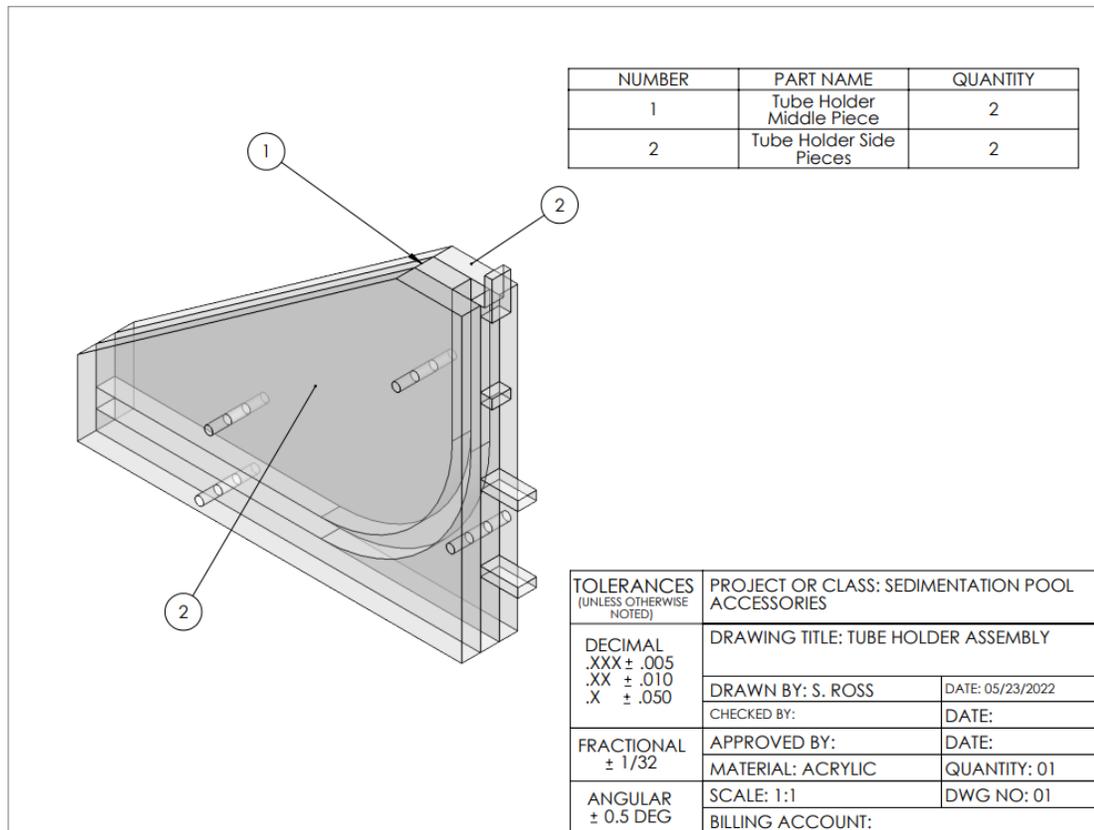
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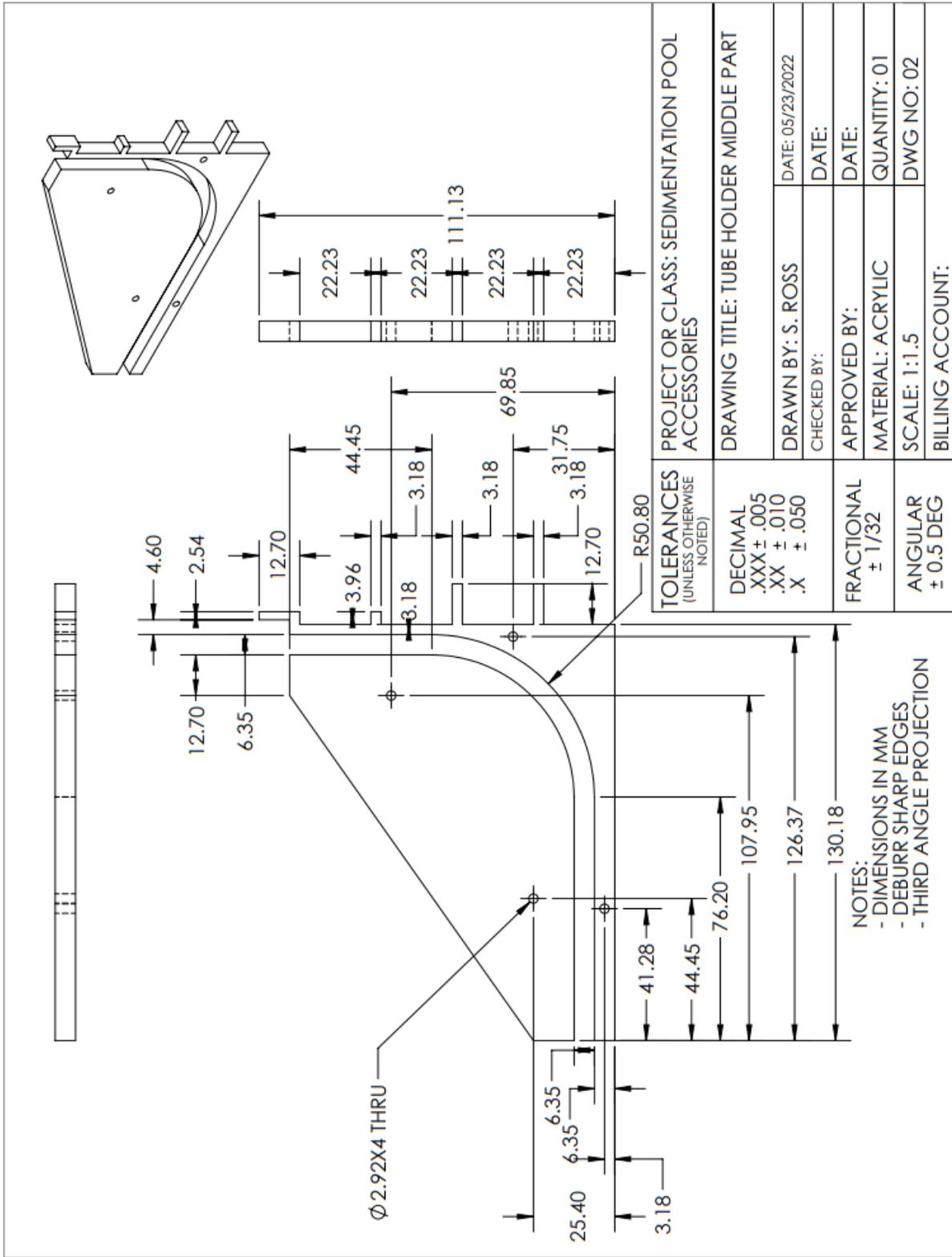
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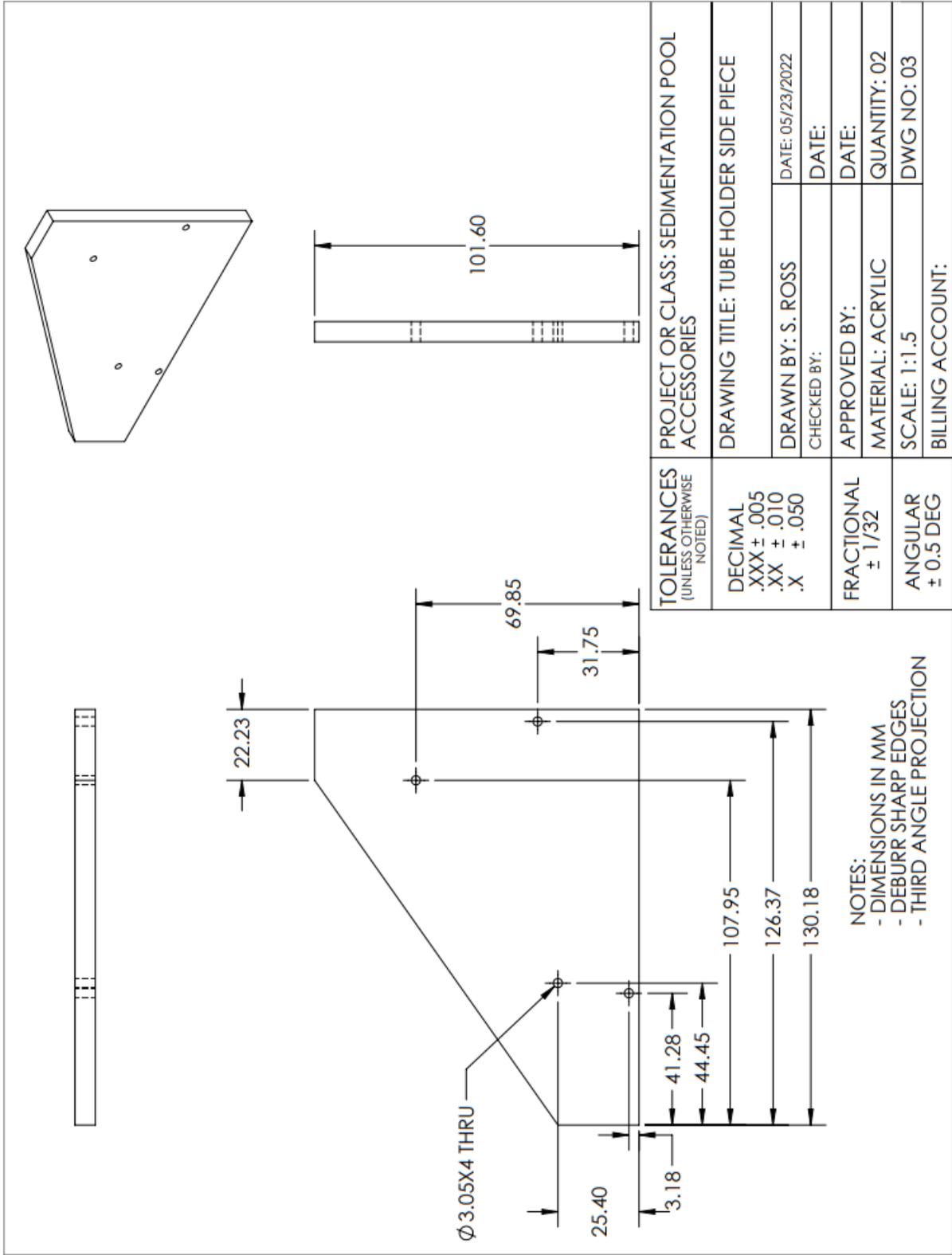
## Appendix A

### TUBE HOLDER DRAWING PACKET

To aid in creating an initial horizontal fluid profile for the slurry feed, an attachment for the pegboard needed to be created to hold the outlet of the tube horizontally beneath the water. The following design was developed, where the four main pieces were sandwiched together using short acrylic dowels and a solvent adhesive.







PROJECT OR CLASS: SEDIMENTATION POOL ACCESSORIES	
DRAWING TITLE: TUBE HOLDER SIDE PIECE	
DRAWN BY: S. ROSS	DATE: 05/23/2022
CHECKED BY:	DATE:
APPROVED BY:	DATE:
MATERIAL: ACRYLIC	QUANTITY: 02
SCALE: 1:1.5	DWG NO: 03
BILLING ACCOUNT:	

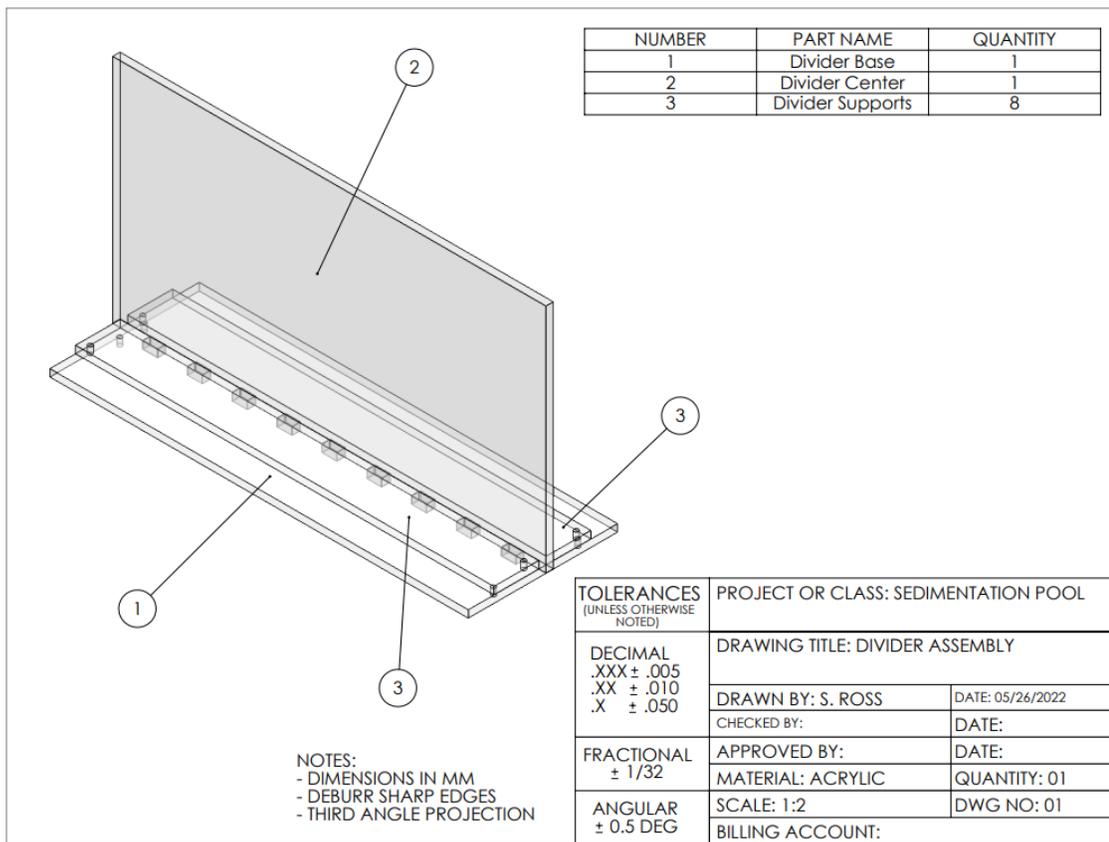
TOLERANCES (UNLESS OTHERWISE NOTED)
DECIMAL .XXX ± .005 .XX ± .010 .X ± .050
FRACTIONAL ± 1/32
ANGULAR ± 0.5 DEG

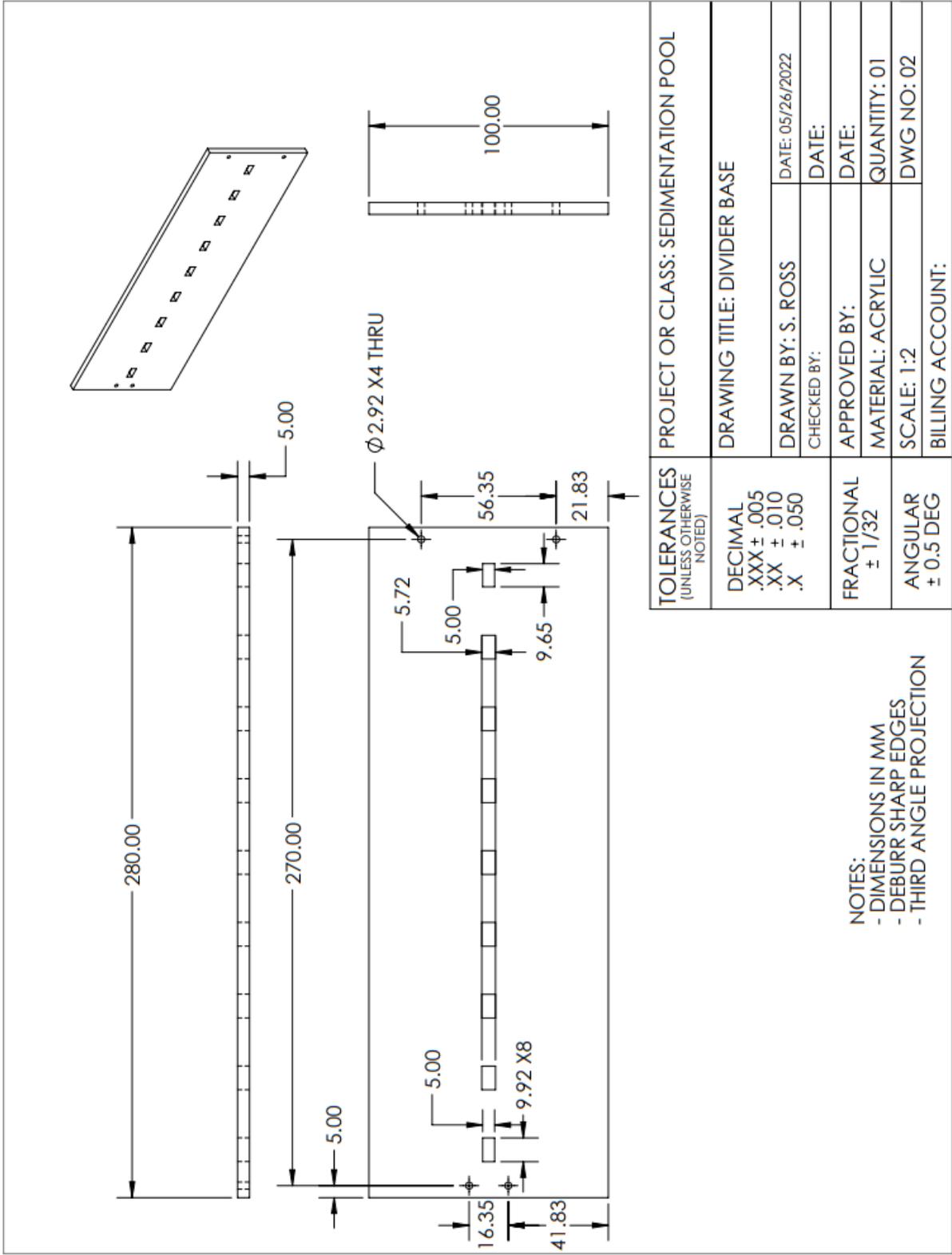
- NOTES:
- DIMENSIONS IN MM
  - DEBURR SHARP EDGES
  - THIRD ANGLE PROJECTION

## Appendix B

### DIVIDER DRAWING PACKET

A divider was designed and manufactured to keep the NMC and carbon deposits separated throughout operation. Box joints were created to support the portion of the divider that protrudes upwards from the base, and many supports were designed for reinforcement if needed.





TOLERANCES (UNLESS OTHERWISE NOTED)	PROJECT OR CLASS: SEDIMENTATION POOL		
	DECIMAL XXX ± .005 .XX ± .010 .X ± .050	DRAWING TITLE: DIVIDER BASE	
FRACTIONAL ± 1/32	DRAWN BY: S. ROSS	DATE: 05/26/2022	
ANGULAR ± 0.5 DEG	CHECKED BY:	DATE:	
	APPROVED BY:	DATE:	
	MATERIAL: ACRYLIC	QUANTITY: 01	
	SCALE: 1:2	DWG NO: 02	
	BILLING ACCOUNT:		

NOTES:  
 - DIMENSIONS IN MM  
 - DEBURR SHARP EDGES  
 - THIRD ANGLE PROJECTION

