Summer 2018

CONTINUOUS FLOW PROCESS FOR RECOVERY OF METAL CONTAMINANTS FROM INDUSTRIAL WASTEWATERS WITH MAGNETIC NANOCOMPOSITES

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CONTINUOUS FLOW PROCESS FOR RECOVERY OF METAL CONTAMINANTS FROM INDUSTRIAL WASTEWATERS WITH MAGNETIC NANOCOMPOSITES

by

David Layton Hutchins

A dissertation submitted in partial fulfillment of the requirements for the degree of

Doctor of Philosophy:

Materials Science

Montana Tech

2018
CONTINUOUS FLOW PROCESS FOR RECOVERY OF METAL
CONTAMINANTS FROM INDUSTRIAL WASTEWATERS WITH
MAGNETIC NANOCOMPOSITES

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B.S. Environmental Engineering, Montana Tech, Butte, Montana, 2014

Dissertation
presented in partial fulfillment of the requirements
for the degree of

Doctor of Philosophy
in Materials Science

Montana Tech
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May 2018

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Remediation of metal-containing industrial effluents presents both a technical challenge and an economic opportunity. Many industrial waste streams contain low levels of metal ions requiring treatment prior to discharge. Existing treatment technologies are frustrated by disparate compositions and low metal concentrations. Chemical precipitation is effective; however, it requires excessive reagents and discourages selective recovery. Ion-exchange enables recovery, but requires a batch process with extensive operational and maintenance demands, and is rarely implemented in large-scale applications. A continuous flow process capable of selective recovery would present many advantages over existing technologies.

This research examines and develops a continuous flow process for recovering metals from industrial wastewaters with magnetic nanocomposites. The objective of this project was to prove the concept and elucidate the mechanisms, and to demonstrate potential for industrial application. All aspects of this process were investigated and optimized to the extent possible. Specific experimentation focused on the development of magnetic nanocomposite ion exchange media, magnetic collection technology, metal recovery, reactor and process development, and modeling.

An effective ion exchange media was developed with a magnetically susceptible magnetite core, durable silica shell, and polyallylamine functionalization. Metal ion loading behavior was demonstrated and modeled, with rapid kinetics and long-term regeneration potential. An in-line, water-cooled magnetic collection module was developed with collection efficiencies exceeding 98%. A pilot-scale vertical reactor was designed and modeled under steady-state operation. Experiments showed efficacy with surrogate solutions as well as actual mine affected waters. A viable metal recovery process was demonstrated with an annular tangential-flow electrowinning technology.

The experimental results proved that this novel nanocomposite magnetic ion exchange media are an effective and reusable means of metal ion removal. Paired with the innovative electromagnetic collection module, a continuous flow process is made possible with low energy demand and pressure differential. This process is effective and predictable, and scalable to industrial applications. These collective findings substantiate the viability of a continuous flow process for recovery of metal contaminants from industrial wastewaters with magnetic nanocomposites.

Keywords: Wastewater treatment, hydrometallurgy, material science, ion-exchange, adsorption, nanocomposites, separation technology, environmental engineering, metallurgical engineering, magnetic collection, nano-scale magnetite, superparamagnetic
Dedication

This dissertation is dedicated to my mother, who has supported me in all my endeavors, especially education.
Acknowledgements

I would like to acknowledge those who were invaluable in the completion of this research.

First, I would like to express my sincere gratitude to my advisor, Dr. Downey, for conceiving of and securing a research project so important and meaningful to me. His expertise and continued support and guidance made this all possible, and I am forever indebted.

I would like to thank my committee members for their contributions and support. My thanks to Dr. Rosenberg for his expertise and work on the ion-exchange media, along with his assistants, Ryan Latterman and Emile DeLuca. Thanks to Dr. Cox for her work characterizing local waters, along with her team, and especially Rene Schmidt. Thanks to Dr. Huang for his help with modeling, along with Maureen Chorney. Thanks to Dr. Ganesan for his continued support and wise advice.

Many thanks to others who participated in this project. Thanks to Dr. Zodrow, and her student Christina Eggensperger, who helped with particle characterization and membrane distillation. Thank you to my lab assistants Jared Geer, Auva Speiser, and Elizabeth Raiha. Thanks to Thad Haines and Frank Joyce for their work on the automation system. Thanks to Gary Wyss for analytical support. Thanks to the Montana Bureau of Mines and Geology, and Gary Icopini, for help securing water samples.

The research project was funded by the Montana Research and Economic Development Initiative of the Montana University System. Thanks to the Montana Board of Regents and the Office of the Commissioner of Higher Education. (Agreement number 51050-MUSRI2015-01)
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1. Introduction

1.1. Background

Remediation of metal-containing industrial effluents presents both a technical challenge and an economic opportunity. Many industrial waste streams contain low levels of metal ions requiring treatment prior to discharge [1]. Mine affected waters pose a serious threat to the environment in Montana and beyond. Acid rock drainage and dissolved metals and metalloids have contaminated ground and surface waters around the world. An effective means of on-site remediation would eliminate the costs and risks associated with waste transportation and, more importantly, provide a permanent and environmentally responsible solution. Recovery of valuable metals can potentially offset significant remediation costs. Application of conventional water treatment methods is unsuccessful due to disparate compositions and low metal concentrations.

Existing treatment technologies for the removal of metals from industrial effluents each have their own advantages and limitations. Conventional wastewater treatment methods include electrochemical deposition, biological treatment, flotation, adsorption, ion exchange, and, the most common, chemical precipitation. The conceptual formula for chemical precipitation with a hydroxide is:

$$M^{2+} + 2(OH)^- \leftrightarrow M(OH)_2$$  \hspace{1cm} (1)

where M is the metal ion of interest, and complexation with the ligand hydroxide produces the insoluble metal hydroxide product. Precipitation by lime addition is the most widely used process for metals precipitation, given the widespread availability and low cost. Lime addition has many advantages, including simplicity of process, low cost of equipment, and effectiveness
with high metal concentrations. Disadvantages include large amount of precipitant required, slow precipitation, and excessive sludge production. Sludge disposal issues, and the long term environmental impacts, must be considered. Metal recovery from sludges is frustrated by complexation and aggregation of metal precipitates.

Ion-exchange is a proven method to remove dissolved ionic constituents. In this process, an ion in the aqueous phase is exchanged for an ion in the solid phase. The solid phase, or ion exchange media, is insoluble and can be a natural material such as zeolite or a synthetic such as a polymeric resin. These media have functional groups on their surfaces, and charged ions associated with them. These ions have an opposite charge of the functional group, maintaining electroneutrality, and are known as counter ions. Because it is a stable and predictable exchange of unwanted ions for wanted ions, it is an ideal removal process. Ion exchange is widely used for water softening, purification, and decontamination, among other applications. Ion exchange is typically performed as a batch process, requiring large vessels and extensive operation and maintenance efforts [2]. Ion exchange is not widely used in large-scale plants because of these inherent limitations.

Alternatives to conventional batch-process ion exchange exist, but lack widespread or large-scale adoption. Multi-column Continuous Treatment Systems have been proven effective [3] [4]. These systems typically operate in a periodic counter-current mode, with multiple columns arranged in a carousel. The supernate is loaded through several columns in series, with at least one additional column in reserve. As the lead column is saturated, the fresh column is rotated into the series. Carousel systems require extensive operation and maintenance effort, and are limited in capacity.
The potential for a continuous ion exchange process that overcomes the limitations of conventional processes is great. A process capable of selective removal and recovery of target ions would represent a significant advancement in wastewater treatment. A process that is continuous, with low energy demand and low pressure drop, that is amenable to automated control, would be conducive to industrial application.

This research builds on the previous work of Dr. Jerome Downey of Montana Tech and Dr. Edward Rosenberg of the University of Montana. Through a grant from the Montana University system and The Montana Research and Economic Development Initiative (MREDI) a project was conceived to pair Dr. Downey’s work in co-current magnetic ion exchange with Dr. Rosenberg’s ion exchange media.

In 2004, while serving at Hazen Research, Inc. (Golden, Colorado), Dr. Downey participated in a Department of Energy (DOE) Phase I Small Business Technology Transfer and Research (STTR) grant. STTR grants support technological innovation with public/private sector partnerships. This project paired Hazen Research with Dr. Arijit Bose of the University of Rhode Island (URI). Dr. Bose had previously demonstrated a flow-through reactor for magnetic colloidal separation [5]. His initial study examined a two cm diameter, one meter long glass tube with hybrid magnetic units capable of colloidal magnetic affinity separation (Figure 1).
In this initial configuration, the tube rotates along with four sets of permanent magnets. In addition, stationary alternating current solenoids surround the tube. Magnetically susceptible polystyrene beads (2.8 µm) are fed into the system along with non-functionalized latex beads. At a given low flow rate, the system showed collection efficiencies of around 60% and a separation factor of 18.2. This study proved the technical feasibility of magnetic separation within a flow-through system and led to the STTR project.

The DOE STTR project continued the work of Dr. Bose with a focus on magnetic collection of magnetically susceptible ion exchange media. Ion exchange is commonly defined as the exchange of ions of the same charge between a solid and a solution. The solid is typically in the form of a polymer bead, called a resin. Because ion-exchange fosters a stable and predictable exchange of unwanted ions for wanted ions, it is an ideal removal process. Ion exchange is widely used for water softening, purification, and decontamination, among other applications. Ion exchange is typically performed as a batch process, requiring large vessels and
extensive operation and maintenance efforts [2]. A compact, continuous system would present a distinct advantage.

The STTR research project, titled “A Continuous Magnetic-field Reactor for Scavenging Metals from Dilute Wastewater Streams”, was funded and initiated in 2004 [6]. The experimental apparatus implemented many of the elements of Dr. Bose’s initial reactor, including the rotary tube and solenoids. In place of the permanent magnets, DC electromagnets were used. The ion exchange media was a commercially available magnetic ion exchange resin (MIEX) from Orica Watercare.

Researchers constructed two reactors, a one inch inner diameter apparatus at Hazen and a one centimeter inner diameter apparatus at University of Rhode Island. Both incorporated DC electromagnet coils positioned around the tube to create a steady radial magnetic field gradient. The energization cycle is controlled so that the discharge can be switched from one that contains a negligible concentration of particles to one that contains a high particle concentration. This process allows for continuous operation. A schematic of the system is given in Figure 2:

Figure 2: 1st generation magnetic separation system [7]
Each reactor was fed dilute metal-containing solutions at a steady rate. The one cm ID reactor ran at 25 mL/min and the one inch ID reactor ran at 80 mL/min. Samples of the effluent were periodically drawn and analyzed via Atomic Absorption. Tenor declined as a function of time for lead and silver (Figure 3).

![Figure 3: Metal recovery results from 1" reactor [7](image)](image)

As shown, the concentrations declined rapidly and then steadily over the duration. Silver concentrations were reduced dramatically, despite non-specific ion exchange resins. Similar successes in recovery were realized in each apparatus. This Phase I STTR project further demonstrated the technical feasibility of this system.

Dr. Rosenberg’s work in ion exchange media goes back decades, and his patented technologies are commercially proven [8]. He developed silica polyamine materials capable of extracting and separating metal ions from actual mining wastewater samples including the
Berkeley Pit [9] [10] [11]. These materials consist of linear or branched water-soluble chelating polyamines covalently bound to a silica gel support (Figure 4)

![Chemical Structure](image)

**Figure 4**: The silica gel-polymer interface showing the approximate structure of the ligating polymer [8]

These composite materials were synthesized following the procedure described in US patent 5,695,882. The silica gel particles average from 90-105 µm and were treated by several methods to produce different characteristics. WP-1 is a primary amine polymer, and the other two materials are analogous branched polymers with secondary and tertiary amines. The tests demonstrated the effectiveness of these composites in separating metal ions from a mixed media, as seen in these results (Figure 5).
The affinity of the media for metal ions varies according to the metal ion and the solution pH. These characteristics allow for targeted ion removal, either by sequential removal or based on pH variations [8] [12] [13] [14] [15] [16] [17].

### 1.2. Statement of Problem

Metal contaminated wastewaters requiring treatment are found around the world, wherever mining and industry are located. Often, these metals pose a serious threat to human health or the environment. Many of these metals, if recovered, are useful to society and are a valuable commodity. A survey of local abandoned mine sites illustrates the abundance of mine affected waters.
An estimated 6,000 abandoned or inactive mine and milling sites exist in Montana [18]. The Montana Department of Environmental Quality has identified 294 priority sites (Figure 6). Many of these sites have associated adit discharges with a low pH, indicative of acid rock drainage (ARD). Most of these discharges contain metal concentrations exceeding the Safe Drinking Water Act Maximum Contaminant Levels and/or acute aquatic life criteria [1].

The oxidation and leaching of sulfide minerals in mines and mine waste is a primary source of ARD. Acid is produced when these ores are unearthed and exposed to water and oxygen in the atmosphere. The oxidation of pyrite, an iron sulfide mineral, is illustrated in equation 2:

$$2FeS_2(s) + 7O_2(g) + 2H_2O(l) \rightarrow 2Fe^{2+}(aq) + 4SO_4^{2-}(aq) + 4H_+^{+}(aq)$$

The Berkeley Pit is an example of metal laden ARD waters as a consequence of pyrite oxidation. A hundred years of underground mining, followed by decades of open-pit mining and then the decision to allow the pit to flood, left the Berkeley pit with 46.8 billion gallons of acidic water as of 2017 [19]. These waters continue to leach metals from the orebody in contact,
exacerbating the situation. An additional 2.5 million gallons flow into the pit daily, and soon it will reach a critical water level, requiring treatment before discharge. The water contains elevated concentrations of a wide array of metals, including iron, zinc, manganese, copper, aluminum, and cadmium. The remedial plan for the Berkeley Pit, as a part of a federal Superfund site, is chemical precipitation of these metals by lime addition. The metal rich sludge will be pumped back into the pit, without recovery of any of the contaminants, necessitating treatment in perpetuity [20].

In addition to the Berkeley Pit, the abandoned underground works include over 16,000 km of shafts and tunnels now filled with low pH water. These waters are also dominated by sulfides, with elevated concentrations of many metals and metalloids. Beneficial uses of these waters have been explored, with limited success [21].

Existing technologies employed in metals ion removal from water pose significant drawbacks and/or challenges. Most common methods, such as lime addition, exacerbate the challenge of metal recovery. Others, such as traditional ion exchange, are costly and require a batch configuration.

Within the fields of hydrometallurgy and wastewater treatment, nano-adsorbents are a significant emerging technology [22] [23] [24]. The unique properties of these materials are expanding the range of applications. This research examines the fundamental science behind these phenomena, while simultaneously exploring the technology necessary for industrial application.

Significant challenges are encountered when attempting to implement an industrial scale nano-adsorbent metal recovery process. Particle size renders most separation techniques inadequate, filtration requires high pressure and extensive maintenance. Efficient and selective
metal recovery requires a complicated synthesis, and the effort required for production of these particles necessitates long-term cyclical reusability.

1.3. Research Objectives and Scope

A continuous process capable of removing and recovering metals from industrial waste streams has potential to be a significant advancement in wastewater treatment. Previous investigation of novel ion exchange media and magnetically assisted pipeline reactors have shown considerable promise [9] [6]. This research synergizes these findings and represents a significant advancement built upon the previous research of Dr. Downey and Dr. Rosenberg, as well as others. The objective of this project is to prove the concept and elucidate the mechanisms, and also to demonstrate the potential for industrial application. Many researchers are currently examining the potential of similar nanocomposite materials for ion adsorption, however, few are applying this technology in an industrially applicable system [25]. The current flows and pipe diameters being investigated represent a significant scale-up from previous iterations and demonstrate the potential for real-world application. Experiments with real mine water samples at realistic flow rates have the potential to show the system is sized for some applications and can be scaled up for others.

Applications for this technology are abundant, however, for this research, a narrower scope has been defined. Specifically, this project was designed to accomplish the following goals:

1. Conduct an exhaustive literature review of relevant science and technologies.
2. Evaluate potential waste streams and identify target ions. Target ions will be chosen on the basis of availability, ease of removal and recovery, value of commodity, and value of removal. Local mine affected waters will serve as the starting point.
3. Evaluate potential magnetic adsorption media and assist in media selection and synthesis.
4. Design and construct continuous flow process system for implementation of removal and recovery of target ions using the selected adsorption media.
5. Design and construct magnetic collection system capable of highly efficient removal within the continuous flow process.
6. Evaluate and optimize process with consideration to scale-up and real-world application.

1.4. Project Plan

The project plan is ambitious: investigate the viability of metal recovery utilizing nano-scale magnetically susceptible particles in a continuous flow process. All aspects of this process will be investigated and optimized to the extent possible. The following procedure summarizes the strategy for achieving the aforementioned goals, numbered as to correlate with those six goals.

1. Literature review: Establish the state of the art, examine alternative treatment options and identify knowledge gaps.
2. Evaluate waste streams: The effort to analyze local waste streams was led by Dr. Alysia Cox and her team at the Laboratory Exploring Geochemical Engineering and Natural Dynamics (LEGEND) at Montana Tech. These researchers sampled and analyzed 9 underground mine works, the Horseshoe Bend Water Treatment Plant effluent, and 3 wells for potential metals of interest and pertinent parameters [26]. The author would then assimilate these data with available references on ease of removal and recovery, value of commodity, and value of removal.
3. Evaluate adsorption media: Dr. Edward Rosenberg and his team at the University of Montana led the effort to synthesize magnetically susceptible nano-composite adsorption media. Extensive experience and research quickly led to a magnetite core with silica shell and polyallylamine functionalization. The author would assist with feedback on media performance and subsequent refinement. Additionally, the author would explore alternate media and coatings.
4. Design and construct process system: The design and construction of the continuous flow process system was led by the author, and represents the bulk of this research. Using fundamental aqueous process data and process models, a pilot-scale reactor was constructed and tested.

5. Design and construct collection system: Although a component of the overall system, the magnetic collection system was a major undertaking and deserving of a dedicated research plan. A technology was modeled based on fundamental electromagnetics, constructed, tested, and refined by the author.

6. Evaluate and optimize process: All parameters and variables were identified and the applicable ranges established. Other components of the process were investigated and tested for compatibility. Bench-scale studies established fundamental process parameters. An experimental plan was developed in order to assess and model the pilot-scale reactors. Steady state operation of the system is the ultimate desired outcome.

A sequence of the overall process is given here, along with a process flow diagram (Figure 7):

- A slurry of magnetic nanocomposite ion exchange particles is introduced to the wastewater stream at the process starting point. The particles and metal bearing solution flow co-currently.
- Functional groups impregnated on the surfaces of the ion exchange particles bond with metal ions as the particle-laden stream flows through the reactor. Alternatively, the energetic surface of magnetically susceptible particles encourages adsorption of metal and/or metalloid ions. Static mixing components within the pipeline reactor ensure complete mixing and adequate contact.
- The electromagnet captures and retains the nanocomposite particles within the collection module, without impeding the wastewater flow. The metal depleted effluent is routed for discharge. Collection wires are allowed to build up particles to a maximum extent, short of particle breakthrough.
• Valve positions are periodically changed to divert flow through a parallel magnetic module, allowing for continuous operation. Valves and other process controls are manipulated by the automation system which also senses and logs pertinent data such as pH and magnet temperature.

• The electromagnet is de-energized to release the particles, which are subsequently stripped and reconditioned by pH adjustment. The regenerated particles are then returned to service.

• The concentrated metal solution is further concentrated by membrane distillation and the metal recovered by electrowinning.
Figure 7: Schematic Process Flow Diagram of the Continuous Flow Metal Recovery System
1.5. General Findings and layout

This research has demonstrated the viability of metal recovery utilizing magnetically susceptible particles in a continuous flow process. The technology has proved to be robust and scalable with a promising future in industrial application. The technology is novel, combining several emerging technologies into a unique and viable industrial process. This research has made important contributions to the fields of Material Science, Extractive Metallurgy, Wastewater Treatment, and Process Engineering.

This dissertation is organized in a typical fashion; Introduction, Methods, Results, and Conclusions/Discussion. The research encompassed many facets of the overall process, and each facet is examined in detail within this context. Certain aspects of this project did not directly involve the author; however, the research was integral to the overall effort and has been included for thoroughness and reproducibility.
2. Theoretical Considerations

2.1. Literature Review

In addition to investigating Dr. Downey and Dr. Rosenberg’s previous work, an exhaustive literature review was performed. All aspects of the project were investigated including ion exchange, nanomaterials, magnetic separation, acid rock drainage, geochemistry, etc. The following represents an overview of the findings, with a more specific review of the relevant science presented in subsequent sub-sections.

Nano-technology and nano-adsorbents have been a focus of research in recent years, with many advancements in the science and technology [27]. Nanoporous adsorbents have been investigated in the fields of biomedical applications [28], environmental remediation [29] [30], and ion recovery [31].

The unique properties of the nanocomposite ion exchange media utilized in this research render most ion exchange literature insufficient. Traditional ion exchange experimental approaches were investigated [32] [33] [34] [35]. Standard laboratory procedures such as batch studies and column tests will require modification to establish loading characteristic and breakthrough curves.

The geochemistry and water quality of local mine sites was investigated [36]. Acid mine drainage, as a potential source for metal rich waste water, was investigated [37]. Pit lakes and the associated chemistry was investigated [38]. In addition to the aforementioned criteria, low-concentration high-value targets were considered [39].

Separation of magnetically susceptible particles from an aqueous flow has been well studied [40] [41] [42] [43]. Research can be separated into two groups, high-gradient field
separation and low-gradient field separation. More specific aspects will be discussed in detail in subsection 2.4.

The literature review also encompassed tangential topics such as alternative metal recovery and alternate adsorbents. Metalloid and non-metal target ions were investigated. A broad range of applications beyond the scope of this research were considered. These topics and references will be discussed in the Recommendation for future work section.

Alternative treatment methods of metal laden waste waters were thoroughly investigated. Commonly used methods as well as emerging technologies were explored. Methods included, chemical precipitation, enhanced precipitation, ion exchange, adsorption, biosorption, biological treatment, natural attenuation in wetlands, and recovery [44] [45].

As previously discussed, chemical precipitation is by far the most common metals removal strategy. Common precipitants include hydroxides, carbonates, and sulfides. Lime, a hydroxide is the most commonly used. Metals are precipitated as hydroxides through the addition of lime to a pH of minimum solubility. The pH of minimum solubility varies with metals and some complexes can interfere with precipitation. Coprecipitation can be highly effective. Metalloids and metals such as arsenic and cadmium can be coprecipitated with iron or aluminum, adsorbing to the floc. Enhanced precipitation agents such as dimethyl thio carbamate can be used for increased performance. Because of reagent costs, enhanced precipitation is typically employed as a polishing step after traditional precipitation. Disadvantages include large amount of precipitant required, slow precipitation, and excessive sludge production. Sludge disposal issues, and the long term environmental impacts, must be considered. Metal recovery from sludge is frustrated by complexation and aggregation of metal precipitates.
Metals can be removed by adsorption onto natural and synthetic materials such as activated carbon, silica, clays, zeolites, and metal oxides such as aluminum, iron, and manganese oxides [46]. Cation adsorption is favored at higher pH, anions at lower pH. Complexing agents can interfere with adsorption and competing ions can be an issue, reducing loading capacities.

Biosorption is a property of some types of inactive microbial biomass to bind and concentrate some metals [47]. Biosorption is a complex process with adsorption, absorption, ion exchange, and surface complexation mechanisms. Commercialization of biosorption has been limited due to challenges with capacity, selectivity, regenerability, kinetics, and cost.

Another potential biological treatment method is the use of sulfate reducing bacteria [48]. Under anaerobic conditions sulfate reducing bacteria will oxidize organic compounds utilizing sulfate as an electron acceptor, generating sulfide. The sulfide can then react with dissolved metals to form precipitates. This method of treatment is complicated by variable input loads and flow, such as seasonal variability and complex discharges.

None of the previously discussed treatment methods lend themselves to recovery of metals. Treatment technologies such as ion exchange, membranes, and electrolytic techniques allow for recovery. The capabilities and drawbacks of ion exchange were discussed in section 1.1. Membranes are an emerging technology in metals removal [46]. Depending on the size of the particle, various membranes can be used such as membrane filtration, ultra-filtration, nano filtration, or reverse osmosis. These technologies can be extremely effective, however high pressure differentials and susceptibility to fouling have prevented widespread adoption.
2.2. Particle Characteristics

Within the fields of hydrometallurgy and wastewater treatment, nano-adsorbents are a significant emerging technology. The unique properties of these materials are expanding the range of possible treatment strategies. For the purposes of this research, the primary desired characteristics are magnetic susceptibility, size and the associated colloidal stability, and metal ion affinity and functionality.

2.2.1. Magnetic susceptibility

Magnetic susceptibility is a measure of the ease with which a material can be magnetized. It is defined by the relationship:

\[ k = \frac{M}{H} \]  

(3)

where \( k \) is the susceptibility, \( M \) is the mass of the material, and \( H \) is the applied field. Often, specific susceptibility is a more relevant measure:

\[ x = \frac{k}{\rho} \]  

(4)

where \( x \) is the specific susceptibility, \( k \) is the susceptibility, and \( \rho \) is the density of the material.

A highly magnetically susceptible material is required in order to achieve high capture efficiencies. The particles can be ferromagnetic, such as iron or cobalt particles, or they can be ferrimagnetic, with the most common example being magnetite. [49]. Typical ferromagnetic materials include iron, nickel and cobalt and their various alloys. Ferromagnetic materials exhibit parallel alignment of moments resulting in large magnetization, even in the absence of a magnetic field (Figure 8).
Ferromagnetic materials have two distinct characteristics; spontaneous magnetization and the existence of a magnetic ordering temperature. The spontaneous magnetization is the net magnetization in the absence of a field. The magnitude of this magnetization at absolute zero is dependent upon the spin magnetic moment of electrons. The saturation magnetization ($H_{\text{sat}}$) is the maximum induced moment that can be obtained in a magnetic field. Saturation magnetization is an intrinsic property that is independent of grain size but dependent on temperature. A typical plot of magnetization vs applied magnetic field of magnetite plateaus at a maximum magnetization of approximately 90 ampere meter$^2$/kilogram (Figure 9).
Oxides, such as magnetite, and some other ionic compounds can exhibit a more complex magnetic ordering than the parallel ordering seen in ferromagnets. One variety of this ordering, ferrimagnetism, is observed in magnetite. The magnetic structure is composed of two magnetic sublattices separated by oxygen anions. This arrangement is attributed to magnetite’s spinel structure. The spinel structure of magnetite consists of oxygen anions in a cubic arrangement with iron in tetrahedral and octahedral sites. The structural formula for magnetite is $[\text{Fe}^{3+}]A[\text{Fe}^{3+},\text{Fe}^{2+}]B\text{O}_4$. This arrangement is known as an inverse spinel (Figure 10). The side view of the inverse spinel structure is shown on the left. The illustration on the right shows the top view with B-termination on the surface in the [100] plane. The black square marks the unit cell. The B-termination consists of oxygen and Fe$_B$ (+2 and +3 charged Fe ions in equal numbers). Studies have suggested the presence of oxygen vacancies at the B-terminated surface [50], potentially explaining high surface energies and adsorption potential.
The tetrahedral and octahedral sites form the two magnetic sublattices, in an antiparallel orientation. This orientation produces an ordering with the majority of moments aligned and the minority anti-parallel (Figure 11).
This anti-parallel magnetic ordering is responsible for the high magnetization measured in magnetite, at around 90-92 Am²/kg. As compared to a ferromagnetic material like pure iron, at 218 Am²/Kg or a ferrimagnetic material like pyrrhotite at 20 Am²/kg, magnetite has a reasonably high magnetization. This susceptibility is in contrast to hematite, Fe₂O₃, with its antiferromagnetic orientation, in which the magnetic moments are equal but opposite and the net moment is zero.
Other theoretical considerations of these magnetic materials include the Curie temperature, hysteresis and stability in an aqueous solution. The Curie temperature is the temperature at which thermal energy overcomes the electronic exchange forces and produces a randomizing effect. The magnet is ordered below this temperature and disordered above it. For this research, a material with a Curie temperature well above typical operating parameters is required. Magnetite has been shown to have a Curie Temperature between 575 and 585°C. A typical plot of magnetization vs. temperature is shown in Figure 12.

Ferromagnets can retain a memory of an applied field after it is removed. This behavior is called hysteresis and a plot of the variation of magnetization with magnetic field is called a hysteresis loop. The initial susceptibility (X₀) is the magnetization in fields on the order of the Earth’s field, approximately 50-100 µT. Another property of hysteresis is the coercivity of remanence (Hᵣ). The coercivity of remanence is the reverse field which, when applied and then removed, reduces the saturation remanence to zero. A typical hysteresis loop with some explanation is shown in Figure 13.
It is important to note the hysteresis parameters are not solely intrinsic but depend upon temperature, stresses, and of great importance to this research, grain size. Superparamagnetism of nano-sized magnetite is well established \[51\] \[52\]. Paramagnetic materials are magnetically susceptible but retain no permanent magnetism. The paramagnetic nature of the nanoparticles is crucial to this application, as the particles must be easily dispersed in the flow but also easily collected by the electromagnet. Once released from the de-energized magnet, the particles must re-dispersed with no remaining magnetism to induce agglomeration. A simplistic comparison of the hysteresis loops of a ferromagnet and those of a paramagnet and superparamagnet can be superimposed on a single plot (Figure 14).

**Figure 13: Hysteresis loops with explanation [92]**

When driving magnetic field drops to zero, the ferromagnetic material retains a considerable degree of magnetization. This is useful as a magnetic memory device.

The driving magnetic field must be reversed and increased to a large value to drive the magnetization to zero again.

The hysteresis loop shows the "history dependent" nature of magnetization of a ferromagnetic material. Once the material has been driven to saturation, the magnetizing field can then be dropped to zero and the material will retain most of its magnetization (it remembers its history).
As is shown, the ferromagnet has a distinct loop and as the field is reduced to zero the residual magnetization remains. The paramagnet does not retain magnetization, but the susceptibility is relatively small. The superparamagnet has a large susceptibility with no residual magnetization when the field is eliminated.

Magnetite possesses all of the desired magnetic susceptibility characteristics: high magnetic susceptibility, high Curie temperature, and superparamagnetism. In addition, it has been well studied and characterized, is inexpensive, and is readily available. These qualities have led many researchers to choose magnetite as a core material or stand-alone adsorption media.
2.2.2. Colloidal Stability

Ideally, the particles will be individually stable in solution, with full, homogenous dispersion, or colloidal stability. Factors such as size, morphology, and surface charge must be examined in order to ensure colloidal stability. A colloid is typically defined as any particle that has a linear dimension between $10^{-9}$ m and $10^{-6}$ m (1nm-1µm) [53]. Nano-scale particles often exhibit colloidal stability despite their density, due to electrical properties.

The predominant electrical property of fine particles is surface charge. This charge contributes to their stability, causing particles to remain in suspension without aggregating. Surface charge may arise from several sources, with four predominant mechanisms: isomorphous replacement, structural imperfection, preferential adsorption of specific ions, and ionization of inorganic groups on the surface. A negatively charged particle in natural water will accumulate positively charged counter-ions near the surface in order to satisfy charge neutrality. A layer of these cations will bind tightly to the surface through electrostatic and adsorptive forces and is known as the Helmholtz layer. Outside of the Helmholtz layer, the net negative charge attracts a layer of non-fixed, predominantly positively charged, ions. This layer, known as the diffuse layer, extends out into the solution until the potential of the surface charge is neutral. Within this layer, the cations and some anions move about in a Brownian motion. Together these layers (Helmholtz and Diffuse) are known as the electrical double layer (EDL). The characteristics and behavior of the EDL are important in understanding the stability and adsorptive behavior of the particles employed in this research.

Colloidal particle stability in water is governed by the balance between the repulsive electrostatic force and the attractive van der Waals force. The electrostatic repulsion is a function of the net negative surface charge discussed previously. The magnitude of this charge will depend upon not only the charge of the particle, but also characteristics of the solution. The
attractive van der Waals forces are caused by synergistic electric and magnetic fields. While these attractive forces may be strong enough to overcome the repulsive forces, stability will be achieved if the EDL extends farther into the solution than the van der Waals forces. On the other hand, if the EDL is not sufficiently extended, particles will aggregate as a result of Brownian motion and will remain attached due to the van der Waals forces. This balance of forces in particle-particle interactions is known as DLVO theory after the scientists who developed it: Derjaguin, Landau, Verwey, and Overbeek.

The effects of ionic strength and counter-ions are of particular interest in this study. Ionic strength has a dramatic effect on EDL thickness, shrinking it with increased strength and valence. When the EDL is compressed to less than approximately 10 Å, attractive forces will dominate. Metal rich wastewaters, considered potential candidates for treatment with this process, will likely have ionic strengths necessitating this consideration. The charge of counter-ions in the solution is also a factor in the compression the EDL, and is proportional to the sixth power of the charge of the ion.

A complex set of equations and considerations are required to predict the ability/ inability of small particles to aggregate in solution and then to precipitate out of solution, but in general, with two spheres of the same radii, the Derjaguin approximation is used to calculate the repulsive forces:

\[ V_r = (64\pi a) \frac{n k_{\text{boltz}} T}{\kappa^2} \gamma_1 \gamma_2 \exp(-\kappa H_0) \]  

where \( V_r \) is the net repulsive force in units of interaction energy per unit surface area, \( a \) is the radius, \( n \) is the charge, \( T \) is the temperature, \( \kappa \) is the thickness of the double layer, \( H_0 \) is the separation distance, and \( \gamma_1 \), and \( \gamma_2 \), are the surface energies of the two different interacting
surfaces. When these forces exceed the attractive van der Walls forces, colloidal stability is expected. By these simplified assessments, particles in the size regimes targeted in this research would be expected to exhibit colloidal stability.

Colloidal stability, however, does not imply a static behavior. Though homogeneous on a macroscopic level, the fluid will undergo continuous fluctuation at the molecular level. These fluctuations result in continually varying pressures and densities, which cause displacement and motion of small particles. The displacements will be completely random, reflecting the random nature of the variations. These random movements are called Brownian motion, and are an important mechanism in diffusion in a liquid, and essential to adsorption.

Sedimentation occurs when gravitational forces exceed the buoyant and viscous forces. Larger particles will diffuse more slowly and will tend to sediment. Consider the particle, with volume \( V \) and density \( \rho \), illustrated in Figure 15

![Figure 15: Schematic of forces acting on a particle](image)
Where $F_v$, $F_b$, and $F_g$ are the viscous, buoyant, and gravitational forces, respectively.

Stokes showed that for a spherical particle, the stationary-state sedimentation velocity is given by:

$$V = \frac{2}{9} \frac{R^2 (\rho_2 - \rho_1) g}{\eta}$$

where $V$ is the velocity vector, $R$ is the radius of the particle, $\rho_2$ and $\rho_1$ are the densities of the particle and the fluid, respectively, and $\eta$ is the coefficient of viscosity. For example, if a 30 nm spherical particle of magnetite is suspended in water at 20°C, the velocity calculated is $9 \times 10^{-9}$ m/s. A settling velocity this slow would be overcome by the forces associated with Brownian motion and would be expected to stay aloft.

Other, non-DLVO factors must be considered as well. Coatings can play an important role, altering size and surface characteristics. Surfactants can dramatically affect surface energy. Steric repulsion caused by polymer coatings can aid in effective dispersion and stability.

Within the context of this research, colloidal stability is preferred. Aggregation is undesirable in this adsorption application for two reasons. First, aggregates have a lower specific surface area, limiting adsorption sites. Second, aggregates may tend to sediment, limiting thorough contact and preventing effective processing [54].

### 2.2.3. Functionality

Nano-scale particles offer many advantages for ion separation, primarily based on their high surface area to mass ratio and colloidal stability. These materials can provide ample surface area, even when dispersed at low volume fractions. For example, consider a sphere of iron oxide with a radius of one cm, as compared to the same volume of an array of nano-scale iron oxide particles with a radius of 10 nm. The larger sphere has a surface area of $1.26 \times 10^2$ cm$^2$, while the
nano-scale particles occupying the same volume would have a collective surface area of $1.26 \times 10^9$ cm$^2$. The larger sphere has a surface energy of $9.07 \times 10^{-5}$ J, while the nano-scale particles occupying the same volume would have a surface energy of $9.07 \times 10^3$ J. Therefore, functions such as adsorption that rely on surface area and surface energy are greatly enhanced by media in this size regime.

In general, traditional ion-exchange media are imparted with four categories of surface functionalization: strong-acid cation, weak-acid cation, strong-base cation, and weak-base cation. The distinctions are based on the pK values; for example, a strong-acid cation exchanger has a low pK ($<0$) and will readily exchange a proton over a wide pH range. On the other hand, a weak acid cation exchanger will have a higher pK value (4-5) and will not readily exchange at a pH below 6.

This research has focused on two polymer surface functionalizations, poly(allylamine) (PAA) and poly(ethyleneimine) (PEI). Both polymers are known to exhibit acceptable metal ion capacities. Their application and performance will be discussed in the results of particle synthesis section.

2.2.3.1. Metal Selectivity

Ligands incorporated on the surface of adsorption media can impart selectivity of target ions. Selectivity is primarily based upon charge-to-radius ratios of the ions in solution. High valence metals typically have the strongest affinity, followed by divalent metals, and then the alkali metals. Many published works have examined the relative affinity for metals of the same charge, with increasing Lewis acidity (and decreasing size) being the predominant factor. The Irving-Williams series is of particular interest, predicting relative stability of complexes formed
by transition metals [55]. The series shows that the stability increases across the period, with a maximum stability at copper, as defined here:

$$\text{Mn(II)} < \text{Fe(II)} < \text{Co(II)} < \text{Ni(II)} < \text{Cu(II)} > \text{Zn(II)}$$

The functionalization of these composites with base amines provides little selectivity for target ions. It is possible to modify these amines with ligating groups, leading to specific metal selectivity and avoidance of complex base regeneration. For instance, an acetate functionalization would impart an affinity toward Cu(II), Ni(II), Zn(II), and Co(II), in that order. Acetal functional groups would also allow effective adsorption at lower pH values. A schematic of silica with surface PEI and PAA with acetal functionalization is shown in Figure 16:

![Figure 16: Schematic of PEI (left) and PAA (right) with acetal functionalization [95]](image)

Other functionalization paths may produce even more selective groups. For instance, CuWRAM is a picolylamine developed by Dr. Rosenberg that has been shown to effectively remove copper (II) in the presence of other competing ions such as iron (III). This media was demonstrated as part of the Mine Waste Technology program as effective in real wastewaters such as Berkeley
Pit water [10]. A schematic of the CuWRAM structure chelating a copper ion is shown in Figure 17.

![Figure 17: CuWRAM functionalization chelating a copper ion [10].](image)

### 2.2.4. Ion-exchange vs Simple Adsorption

In addition to ion-exchange adsorption mechanisms, simple adsorption was considered within the context of this research. Adsorption is the mass transfer of a constituent in an aqueous phase onto the surface of a solid. These dissolved species are concentrated on the surface of the solid by chemisorption or physical adsorption. Physisorption is a weak adsorption through Van der Waals forces with no involvement of the electronic structure. Chemisorption involves the formation of new bonds. The most common adsorption media, activated carbon, is frequently used in removal of organic contaminants, but also has potential with metals. Adsorbents typically have porous structure and a high specific surface area. Nano-scale adsorbents, with their high surface area to volume ratio, are especially of interest.

Metal oxides are ubiquitous in nature, composing the majority of the Earth’s crust. These oxides are often found to be effective adsorbents [56]. Charged ions on the surfaces of these
oxides lend themselves to an acid-base description of the adsorption processes. An acid, by the Lewis definition, is a substance that can accept an electron, and a base is a substance that can donate an electron. Oxide surfaces may be described as an ordered array of adsorption sites. Positively charged metal ions are electron deficient and are an adsorption site for a molecule with excess electrons. Conversely, the oxygen atoms are an attractive site for electron-accepting Lewis acid molecules. The relative strength of the chemisorption bonds at the surface of metal oxides varies with several factors, including charge, degree of coordinative unsaturation, and geometric considerations.

Uncoated magnetite is known to be an effective adsorption media [57] [58]. Nano-scale magnetite particles are unique in their ability to adsorb a wide range of cations and anions. Magnetite is amphoteric, meaning it is capable of reacting as an acid and a base, as previously discussed. Solution pH is an important controlling parameter, with metal adsorption dependent on proton concentration. It has been shown for copper, the higher the proton concentration, the lower the efficiency of copper (II) removal [58]. With a higher pH a greater number of deprotonated sites are available, resulting in higher uptake.

2.3. Nanocomposite Synthesis

Synthesis of the nanocomposite adsorption media requires three general steps; synthesis of the magnetically susceptible core, polymeric coating of the core, and functionalization of the surface. Magnetite synthesis can be achieved by several methods, with the three most common described here. The most basic method of synthesis is through size reduction. Larger particles or bulk material are reduced through comminution, typically by grinding in a ball mill within a dispersant and in the presence of a surfactant. This method is a simple and effective; however, it
is time consuming and energy intensive. Another method is organometallic decomposition, where an organometallic compound is dissolved in a solvent and heated to an elevated temperature. The organometallic species dissolves and the insoluble metal precipitates. Magnetic particles have been produced from this method, such as magnetite from iron pentacarbonyl. The most common method of synthesis, due to its simplicity and low cost, is chemical coprecipitation.

Coprecipitation of magnetite nano particles can be achieved by basic precipitation of an aqueous solution of iron (III) chloride and iron (II) chloride in a 2:1 molar ratio, with a precipitating agent. This forms the spinel structure of magnetite discussed in detail in subsequent sections. The stoichiometry of this reaction is shown in equation 8:

$$2FeCl_3 + FeCl_2 + 8NH_4OH \rightarrow Fe_3O_4 + 8NH_4Cl + 4H_2O$$

(8)

In this case ammonium hydroxide is the basic precipitating agent, usually added in excess. Many factors affect the character of the particles, including reagent concentration, temperature and pH.

Polymeric core coating and surface functionalization are steps in the process with nearly infinite possible variation. Rather than attempt to summarize the possibilities, the path that led to the final magnetic nanocomposite (MNC) utilized in this research is given in the Results section. In addition, alternative coatings and functionalizations are discussed in the Recommendations for future work section.

### 2.4. Magnetic Collection

In the context of this research, magnetic collection involves the application of a magnetic field gradient causing movement of magnetically susceptible particles toward the region of
higher field strength, allowing separation from the nonmagnetic solution. This movement is known as magnetophoresis.

### 2.4.1. High-Gradient Fields

Conventional methods of magnetic separation, such as a drum separator for mineral processing, are not effective for separation of nano-scale ferromagnetic materials from a liquid medium. High gradient magnetic separation has been developed for effective separation of this class of materials [59]. High gradient magnetic separation typically consists of an electromagnet with a core of magnetically susceptible wires. This arrangement creates high field gradients around the wires, attracting the particles to the surface. The force exerted on the particle is given by Equation 9

\[
F_m = \mu_0 V_p M_p \cdot \nabla H
\]

where \(\mu_0\) is the permeability of free space, \(V_p\) is the volume of the particle, \(M_p\) is the magnetization of the particle, and \(H\) is the magnetic field at the location of the particle. This force must exceed all competing forces, including fluid drag, gravitational, and inertial.

### 2.4.2. Particle Build-up

Separation of magnetically susceptible particles from an aqueous flow has been thoroughly studied [40] [41] [42] [43]. The strength of the field decreases rapidly with the distance from the surface of the wire. Attention must be given to the effects of particle buildup on the wire, and the subsequent decreased field strength at greater distance. The work of Moeser, et al is of particular interest in the context of this research. Published work such as *High-gradient Magnetic separation of Coated Magnetic Nanoparticles* defined the relationship between
magnetic field strength, particle size and magnetic susceptibility, and flow velocity and viscosity [59]. Moeser developed a theory that describes the static buildup of particles around collection wires, with fluid drag and diffusion as the primary forces opposing capture in high and low flow regimes, respectively.

![Figure 18: The High-Gradient Magnetic Model System [60]](image)

2.5. Process Modeling

Reactor modeling

The co-current pipeline reactor can most closely be characterized as a plug flow reactor (PFR). A PFR is an ideal reactor in which fluid moves through the process as a plug and does not mix with the fluid elements in front or behind it. In other words, the PFR exhibits perfect radial mixing and negligible longitudinal mixing. Thus, the composition at any point and time is identical to the composition in a completely mixed batch reaction after the same period of time. Of course, this idealized model is not entirely accurate. Static mixers within the pipeline will create tortuous paths and turbulence, and subsequent mixing. In addition, the liquid and solid
phases, the solution and particles, may not travel at identical velocities. Additional complexity is encountered in the reactor once the particles are immobilized and the solution continues to flow.

A quantitative analysis of the process can be accomplished through a mass balance. The solution to be treated, be it a laboratory produced surrogate solution or an actual sample of mine water or industrial effluent, should be analyzed and the concentration and total load of the metal species of interest quantified. Likewise, the dose of adsorption media and quantity of carrier fluid will be known. Flow should be carefully monitored, instantaneously as well as in total. Subsequent processes, such as magnetic collection and stripping should be treated with the same precision. In the end, all constituents should be accounted for, within reason.

**Adsorption modeling**

In order to generate predictive models of the process, kinetic models may be developed in the form of isotherms. These isotherms describe the complex heterogeneous solid/liquid reactions, including the diffusion into and out of the solid media and the diffusion into and out of the liquid. Due to the complexity of these systems, basic kinetic studies fall short and empirical equations and parameters must be employed. The two most common theoretical frameworks are known as the Langmuir and Freundlich models.

The Freundlich model applies to a heterogeneous surface where multiple layers may be deposited and maximum capacity cannot be achieved. The general equation is given in Equation 10:

$$ [S \equiv A] = m[A_{solution}]^n $$

(10)

where $[S \equiv A]$ denotes the surface concentration of of a site, S, occupied by the adsorbate A, and $[A_{solution}]$ denotes the concentration of A in solution. Parameters m and n are empirically derived from experiments, estimated using the linear Equation 11:
\[ \ln[S \equiv A] = \ln(m) + n\ln[A_{solution}] \] (11)

The Langmuir model supposes monolayer deposition upon a homogeneous surface. The capacity can be expressed as the sum of the empty and occupied sites, as shown in Equation 12:

\[ [S \equiv T] = [S \equiv max] = [S \equiv] + [S \equiv A] \] (12)

where \([S \equiv T]\) denotes the total number of sites, and \([S \equiv]\) denotes concentration of empty sites.

A typical equation for an equilibrium constant for adsorption, \(K_{ads}\), is given as

\[
K_{ads} = \frac{[S \equiv A]}{[S \equiv] \times [A]} \] (13)

where \([A]\) is the concentration of adsorbate in the solution phase. Rearranging equations 12 and 13, and, by convention, replacing \([A]\) with \(C_e\), \([S \equiv]\) with \(q_e\), \([S \equiv T]\) with \(q_{max}\), and \(K_{ads}\) with \(b\), Equation 14 is generated.

\[
\frac{C_e}{q_e} = \frac{1}{bq_{max}} + \frac{C_e}{q_{max}} \] (14)

From a plot of experimental data, \(C_e\) versus \(C_e/q_e\), the constants \(q_{max}\) and \(b\) can be computed from the slope and intercept of the resulting line.

The Freundlich and Langmuir models, as well as others, should be investigated for best fit with empirical data, however, ion exchange will typically follow the Langmuir model with a fixed number of sites available.

2.6. Scalability

Scalability of the system is of importance for the eventual industrial application. Similitude must be established for not only the geometry of the pipeline, but for the flow and the magnetics. The magnetics pose the most significant challenge. In the context of magnetic
collection, the fluid drag, which is primarily a function of velocity, and the magnetic field strength must be considered. In order to keep velocities low, the cross-sectional area of the flow must be maximized. However, as the cross-sectional area is increased the magnetic strength decreases inversely proportionally to the radius cubed. In order to maintain higher field strengths, electromagnetics with more windings and higher current must be utilized, subsequently increasing ohmic heating.

As scale-up and similitude are explored, several pertinent dimensionless numbers should be considered and potentially modified to the specific scenario. Dimensionless numbers, or groups, relate various parameters within complex fluid dynamics across scales. Therefore, the data collected from a model in the laboratory can be applied directly to a scaled-up prototype.

Three of the most common and relevant dimensionless numbers are given in Table I:

<table>
<thead>
<tr>
<th>Name</th>
<th>Π-group</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reynolds</td>
<td>( \frac{\rho LV}{\mu} )</td>
<td>( \frac{\text{Kinetic Force}}{\text{Viscous Force}} )</td>
</tr>
<tr>
<td>Peclet</td>
<td>( \frac{LV}{E} )</td>
<td>( \frac{\text{Solute transfer by advection}}{\text{Solute transfer by axial dispersion}} )</td>
</tr>
<tr>
<td>Froude</td>
<td>( \frac{V}{\sqrt{gL}} )</td>
<td>( \frac{\text{Kinetic Force}}{\text{Gravitational Force}} )</td>
</tr>
</tbody>
</table>

where \( \rho \) is density, \( L \) is length, \( V \) is velocity, \( \mu \) is viscosity, \( E \) is the dispersion coefficient, and \( g \) is the force of gravity.

These three dimensionless numbers allow a direct comparison of forces and phenomenon over different scales. The Reynolds number is important in quantifying the ratio of inertial forces
to viscous forces, and describes the degree of laminar or turbulent flow. Turbulence is a crucial component of mixing and will be relevant in this research. The Peclet number describes the mass transfer mechanisms in adsorption, and is generally used in modeling a fixed bed. Significant modification will be required to apply this ratio to adsorption on colloidal particles in solution. The Froude number is significant, describing the relationship between flow inertia, and velocity, to an external force, in this case, gravity. This ratio is important, as it aids our understanding of the resistance of a submerged object moving through water. The particles used in this research are at the lower limit of size, so a proportionally small particle, with respect to the channel diameter, is not possible.

These dimensionless numbers will also be helpful in assessing the efficacy of magnetic capture over scales. For instance, the Reynolds number may be modified with velocity replaced with the magnetophoretic velocity [25]. The resulting calculation gives insight into particle behavior within a magnetic field: at >1 motion will be magnetophoresis dominated, at <1 viscosity dominated. A similar modification may be performed upon the other dimensionless numbers, and they may be compared across scales.
3. Experimental Materials, Apparatus, and Procedure

3.1. Particles

3.1.1. Synthesis

Particle synthesis was performed by Dr. Rosenberg and his assistants at his laboratory at the University of Montana. The following synthesis protocol represents the final product and was the culmination of many alternative paths discussed in the results section.

Silica coating of Fe₃O₄ nanoparticles

Eighty grams of nanoparticles (NPs) were suspended in one liter of 2-propanol in a beaker and sonicated in a bath sonicator for 15 minutes while occasionally stirring before being placed in a 12 L three-neck round-bottom flask. While stirring (overhead stirrer, 285 RPM) 3 L of 2-propanol and 1 L of deionized water were added, followed by 200 mL of 28% ammonium hydroxide solution. After stirring for 5 minutes, 70 mL of tetraethyl orthosilicate (TEOS) was added. The suspension was stirred at room temperature for three hours under nitrogen atmosphere. A permanent magnet was carefully placed on the bottom side of the flask to collect the NPs and the supernatant was removed using an aspirator vacuum apparatus (Figure 19). Multiple portions (~800 total volume) of 2-propanol were used to remove the NPs from the flask and then collected in a beaker. The NPs were washed with 2 x 300 mL of 2-propanol and 2 x 250 mL of acetone by collecting the NPs on the bottom of a beaker with a permanent magnet and discarding the supernatant. A stream of air was used to evaporate most of the residual acetone before drying the NPs in a vacuum chamber. Typical isolated yield was 90-100g.
Surface functionalization with 3-chloropropyltrimethoxysilane (CPTMS) and methyltrimethoxysilane (MTMS)

One hundred grams of silica-coated Fe$_3$O$_4$ nanoparticles were suspended in 800 mL of toluene and stirred (overhead, 200 rpm) and sonicated in a bath sonicator for 20 minutes in a 3 L three-neck round bottom flask under ambient conditions (Figure 19). 350 mL of MTMS and 50 mL of CPTMS (7:1 volume/volume ratio) were dissolved in 400 mL of toluene before adding to the nanoparticle suspension. After stirring for three hours, the NPs were washed with 2 x 300 mL of toluene and 2 x 250 mL of acetone by collecting the NPs on the bottom of a beaker with a permanent magnet and discarding the supernatant. A stream of air was used to evaporate most of the residual acetone before drying the NPs in a vacuum chamber. Typical isolated yield was ~100 g, depending on the amount of NPs lost during wash steps.
Surface functionalization with poly(allylamine) polymer

One hundred grams of MTMS/CPTMS-functionalized NPs were added and suspended in 100 mL of methanol followed by the addition of 350 mL of aqueous 15% wt/wt poly(allylamine) solution. NPs were stirred (overhead, 200 RPM) and sonicated in a bath sonicator under ambient conditions overnight using the same configuration as shown in Figure 19. The NPs were washed with 4 x 400 mL of deionized water and 2 x 250 mL of acetone by collecting the NPs on the bottom of a beaker with a permanent magnet and discarding the supernatant. A stream of air was used to evaporate most of the residual acetone before drying the NPs in a vacuum chamber. Typical isolated yield was 95 g to 97 g, depending on the amount of NPs lost during wash steps.

Preparation of aqueous 15% wt/wt poly(allylamine) solution from PAA-HCl salt.

Twenty five grams of poly(allylamine) hydrochloride (17,500 average MW, Sigma Aldrich) was dissolved in 50 mL of deionized water in a tared beaker containing a magnetic stir bar. The solution pH was adjusted to 12.35 by adding 4M sodium hydroxide solution (~50 mL). Enough deionized water was added to achieve a total mass of 166.50g.

Iron Oxide Nanoparticles

Commercially available iron oxide nanoparticles comprised the core of the composites and served as the subject for dedicated experimentation. Particles were procured from Skyspring Nanomaterials of Huston, Texas. The particles are a magnetite nanopowder with the empirical formula $\text{Fe}_3\text{O}_4$. They present a spherical morphology with an average diameter of 20-30 nanometer (nm), as seen in the micrograph in Figure 20. The vendor reports a surface area of 40-60 m$^2$/g, a bulk density of 0.84 g/cm$^3$, and a true density of 4.8-5.1 g/cm$^3$. The purity is reported as 98+%, with the maximum trace elements shown in Appendix A.
Dispersion

Both the magnetite and coated magnetite particle powders utilized in this research proved challenging to fully disperse in water. Several strategies were attempted with limited success, including sonication, agitation, pH adjustment, and surface modification with surfactants. Each of these methods left agglomerated and floating particles, suspected of entrapping air. After much trial and error, an effective dispersion protocol was established:

- Place powder particles in a one liter vacuum flask. Typical batches thus far have been approximately 40 grams.
- Cover particles with ethanol sufficient to wet all material and agitate.
- Sonicate mixture for 5 minutes.
- Add DI water up to 500 mL.
- Apply vacuum with a pressure of -25 in Hg in order to degas and volatilize excess ethanol.
This method has proven effective; however, the agglomerations are still not entirely dispersed. Additional sonication failed to increase dispersion. Similar degrees of dispersion were observed after multiple load and strip cycles. As long as particles are not allowed to dry they will remain mostly dispersed.

3.1.2. Characterization

Both the functionalized particles from Dr. Rosenberg’s laboratory and the magnetite particles were subjected to numerous characterization analysis. The size, density, morphology, elemental composition, and surface charge were investigated. The following analytical techniques were utilized to this end:

**X-Ray Diffraction**

The structural characterization of raw magnetite was conducted by powder x-ray diffraction spectrometry (XRD) using a Rigaku Ultima IV instrument between 5 and 85° at a scanning rate of 3°/min. Samples were pulverized using a ring-and-puck. PDXL software was utilized to assign a best fit.

**SEM-EDS**

The morphology, topology, size, and elemental composition were investigated by Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM-EDS) with an LEO 1430 VP. The instrument is equipped with an Ametek Ziess 1430 EDAX.

**Particle Size**

The average particle diameters were investigated by Dynamic Light Scattering (DLS) with a Malvern Zetasizer (Mal500018). Solutions of 50mL DI water and particles were created. Initial size measurements were conducted using magnetite particles. One mg particles were
added to 50mL DI water. Mixture was sonicated for 10 minutes and then promptly placed in Malvern Zetasizer to perform size measurement.

**Zeta Potential**

Particle Zeta potentials were measured with the Malvern Zetasizer (Mal500018). Solutions of varying pH were created. For each solution, first, sonicate 20mL DI water with one mg particles. Add drops of 0.1M HCl and 0.1M NaOH to adjust pH. Resonicate the solution before measuring pH to allow for complete mixing.

**UV Vis**

Solutions of varying concentrations of NaCl are prepared: 0M, 0.005M, 0.01M, 0.015M, 0.02M. NaCl is added to DI water and each mixture is sonicated using probe sonication for 10 minutes. Absorbance measurements are taken immediately after sonication using UV-Vis. With the wavelength set at 600nm, an absorbance measurement is taken every minute for 10 minutes.

**Density and settling velocities**

Density was estimated with a mass difference method. Two samples of known volume of fluid were compared, one without particles, and one with a known mass of dry particles dispersed within the solution. Density was then calculated relative to the fluid density.

Settling velocities were investigated in a settling velocity column. A slurry of dispersed particles was added to a 30 cm column full of water and allowed to settle. The process was captured in video. The video and accompanying time stamps were used to identify average settling velocities.

**Magnetics**

An Eriez Davis Tube was utilized to examine the relative magnetic susceptibility of particles. Electromagnetic coil parameters, including resistivity, voltage, and amperage were
measured with a Klein CL2000 multimeter. Magnetic flux was measured with an FW Bell Gauss meter.

**3.1.2.1. Adsorption loading and kinetics**

Batch tests were performed in 20 mL glass scintillation vials. Varying amounts of each resin (100mg, 200 mg, or 400 mg) were weighed into each vial. Three copper solutions were prepared at a concentration of 60 mg/L of copper, using copper sulfate; each scintillation vial was filled with 20 mL of solution. Two solutions were buffered with a 0.1 M citrate buffer to create solutions of pH 5.4 and 6.2; the third solution was not buffered. A total of 45 sample vials were placed on an oscillating shaker table (480 rpm) for 20 hours.

The kinetics of the CMNCs were analyzed using beaker tests. Approximately 100 milligrams of composite was used for each test. An oscillating shaker table (160 rpm) was employed to agitate the resin once the solution was added to the beaker. Two batch tests were conducted, varying only solution concentration (150 and 1500 mg/L Cu). Samples were withdrawn at timed intervals and immediately filtered. The amount of copper adsorbed was measured by atomic adsorption of the depleted solution. All measurements were performed in triplicate and the volume of solution withdrawn was insignificant compared to the total volume of the solution.

**3.2. Magnetic capture**

**3.2.1. Apparatus**

In order to overcome the challenges of magnetic collection in a large internal diameter pipeline, new electromagnet designs were investigated. A ring-shaped electromagnet positioned around the pipeline of sufficient strength would be large, expensive, and require aggressive cooling. A new strategy was investigated: position the electromagnet within the flow. This scheme would allow for close contact with the flow and the wastewater flow would provide
direct cooling to the coil. A model was developed in order to estimate the strength of the magnetic field within the coil. The model is based in part on the Biot-Savart equation for current densities:

$$B_r = \mu_0 \frac{\mu_0}{4\pi} \int \int \int \frac{J(r') \times (r - r')}{|r - r'|^3} dV$$

(15)

where $B_r$ is the strength of the magnetic field, $J$ is the current density, $\mu_0$ is the vacuum permeability, and $r$ and $r'$ are the inner and outer radii of the coil. This equation takes into account the radius of the coil and the total current. However, with a few assumptions a simplified equation may be utilized. If it is assumed that the current flows through a single circular loop of infinitesimal width, and the bulk of the current flows through a loop with a radius half way between the inner and outer radius, the following equation can be derived:

$$B_r = \frac{\mu_0 \cdot N \cdot I}{2 \cdot R}$$

(16)

where $B_r$ is the strength of the magnetic field, $\mu_0$ is the vacuum permeability, $N$ is the number of turns, $I$ is the current, and $R$ is the average radius. The actual mean current has a slightly smaller radius, so this equation will produce a slightly smaller field than in reality. The coils that were produced utilizing this model were tested with a gauss meter and measurements confirmed that the field strength calculated by the model was reasonably close to the measured field strength in the actual system, as measured with a FW Bell 5180 gauss meter.

The first coil design effort sought to produce a minimum 0.8 Tesla field within the annulus. The inner diameter of the collection module (6 inches) and inner diameter of 2 inches to preserve flow characteristics, provided the other design limitations. A coil of copper magnet wire, 16 awg, with approximately 1400 turns was fabricated in house utilizing a custom jig. The
coil proved effective and was utilized for the majority of the vertical magnetic collection tests. All testing was performed at maximum field strength, given the resistance of the coil and the limits of the power supply. The power is provided in a continuous current mode, with the amperage fixed at 11 amps and the voltage varying from 54 to 60 volts, as the temperature and resulting resistance increase. The coil within the collection module is shown in Figure 21.

![Figure 21: In-line electromagnet coil](image)

Experiments described in the literature have shown core material to greatly increase the collection efficiencies [59]. High-gradient fields can be created around wires where magnetically susceptible particles can collect. An arrangement of iron-chromium-aluminum wires was devised parallel to the magnetic field lines as show in Figure 22.
The core material is commercially available and branded Kanthal A. Kanthal A is a ferritic iron-chromium-aluminium alloy (FeCrAl alloy) with high resistivity and good oxidation resistance for use at temperatures up to 1350°C (2460°F). More details on this material are provided in Appendix A.

Collection efficiencies improved with this core material and particles were observed to accumulate on the wires. Subsequent iterations would utilize finer wires in greater numbers in the same configuration with greater collection efficiencies. During a routine experiment performed in July 2016, the coil was destroyed after it was inadvertently left energized without flowing solution to provide coolant. A replacement coil was fabricated with nearly identical specifications and results, and plans were made to integrate more stringent safety measures into the process control system.

After consultation with experts, it was decided to outsource the next two coils. Magnetech Corp was contacted and two coils were commissioned. These coils were similar to the previous two, with one noted upgrade. The entire coil was encapsulated in a protective resin.
In order to prolong life, especially in acidic environments. The finished coil is shown in Figure 23.

Figure 23: Electromagnetic coil from Magnetech Corp.

In order to investigate particle collection efficiencies, an apparatus was designed and built. This system consists of a vertical column approximately 1.6 meter tall with the magnetic collection module positioned near the middle. The column was constructed of Schedule 40 Clear polyvinylchloride pipe, 2 inch inner diameter at the top and bottom with the collection module expanded to a 6 inch inner diameter. Simple gravity flow conveys water at a specified flow determined by the position of a valve at the exit. A schematic of the apparatus is shown in Figure 24.
3.2.2. Experimental Method

The following method was utilized for all magnetic capture experiments. The majority of experiments were performed with 20-30 nm diameter magnetite particle. Some experiments were performed with various magnetic nanocomposites, including coprecipitated, unfunctionalized, PAA functionalized, and PEI functionalized particles. All magnetic nanocomposites were provided by Dr. Rosenberg’s laboratory. All magnetite particles were secured from Skyspring Nano, with the properties previously outlined. The water was tap water.
• The appropriate mass of particles is weighed and dispersed with the dispersion method previously detailed.
• The main valve is closed and the control valve is adjusted to the appropriate flow. The apparatus is filled with water.
• The electromagnetic coil is energized in continuous current mode, set to 11 amps. The voltage is determined by resistance of the coil, it is recorded periodically.
• Simultaneously, the flow is initiated, the timer is started, and the magnetite slurry is added to the top of the column. The effluent is collected in an appropriate vessel I. Water is added to maintain a constant head.
• By visual inspection, determine when all particles have entered the magnetic coil. Various flow rates, and the associated velocities, will result in varying total time for completion. After an additional 60 seconds, the valve is closed and flow ceased.
• The electromagnet is de-energized, and captured particles are allowed to settle. Vessel II is placed to receive the effluent. The valve is reopened and the particle rich effluent is collected. Additional water is used to flush residual particles.
• Particles in vessel I are collected with a powerful permanent magnet in a latex sleeve. The sleeve is removed and the particles are dried in an 85°C oven for at least 6 hours. The particles are weighed.
• Particles in vessel II are allowed to settle and the water is decanted to the extent possible. The remaining slurry is vacuum filtered through a Whatman 1 paper filter, dried and weighed.

The collection efficiency is calculated with the following equation:

$$\eta = \left( \frac{M_i - M_{eff}}{M_i} \right) \times 100$$

(17)

where $\eta$ is the collection efficiency percentage, $M_i$ is the initial mass of particles, and $M_{eff}$ is the mass of particles in the effluent. A mass balance is performed as well, ensuring the sum of the masses in vessels I and II are within ±1% of the initial mass.
3.3. Bench-Scale Experiments

3.3.1. Adsorption within a magnetic field

An experiment was devised to compare adsorption capacities and rates of copper ion adsorption onto magnetite particles, within and without a magnetic field. An apparatus was fabricated in order to complete these experiments, consisting of a 2 inch diameter PVC pipe within a 6 inch diameter PVC chamber. The pipe is positioned vertically with an expansion plug at the bottom and 100 strands of core material attached to the plug, running approximately parallel to the magnetic field. The chamber contains a 6 inch diameter, 4 inch tall electromagnet coil around the pipe. The magnet is submerged in DI water as a coolant.

Scoping experiments were conducted with the following parameters:

- A 325 mL solution of DI water and CuSO₄·5H₂O created with a target of 8mg/L concentration of copper.
- A 1.0 gram sample of 20-30 nm diameter magnetite (Fe₃O₄) particles is covered in approximately 30 mL ethanol and agitated on a shaker table. Following full dispersion, 100 mL of DI water is added and agitated further. The mixture is then placed under vacuum for approximately six minutes or until all off-gassing ceases. The remaining slurry is placed on a shaker table until needed.
- The entire apparatus is placed on a shaker table at 105 RPM. The copper solution and particle slurry are combined in the pipe and a timer is started. A 10 mL sample is retrieved from a point 130 mm from the top of the pipe at exactly 45, 180, and 300 seconds.
• Samples are immediately filtered through a 0.45 µm syringe filter and placed in a 20 mL scintillation vial. It appears the vast majority of particles are removed and adsorption ceases.

• The samples are analyzed via spectrophotometry, using a HACH DR 3900. The HACH TNT 860 method is employed, with a range of 0.1-8.0 mg/L Cu.

• The experiment is conducted in duplicate with all parameters identical except the presence of a magnetic field. When energized, the coil is held at a constant current of eight amps, and a voltage fluctuated from 47 to 54 volts as temperature and resistance increase.

• The pH of the solution and slurry are left as the intrinsic value. The temperature is ambient (≈22˚C) and the heat from the magnet was found to not increase the temperature of the mixture over the duration of the experiment.

Two distinct cores were fabricated and tested in order to further develop the model for reduced effective surface area due to magnetic agglomeration (Figure 25). The first, Core I, is the

![Figure 25: Magnetic cores, I and II](image)
core used in previous experimentation with 200 Kanthal wires. The second, Core II, has 20 wires but is otherwise identical. A clear difference in removal efficiency was shown over a series of six experiments.

3.3.2. Bottle and Shaker-table Tests

Bottle tests were performed with both surrogate and actual wastewater solutions in order to assess adsorption behavior of magnetic nano-composites (MNC) and magnetite particles.

**Copper sulfate:** Early experiments sought to establish total loading capacities of MNCs as well as raw magnetite nano-particles by agitating particles within a copper (II) sulfate solution for 24 hours. Approximately 7.4 grams of each media were added to 450 mL of a DI water and copper (II) sulfate solution in a 500 mL plastic Nalgene bottle. The bottles were sealed and placed on continuous rollers at 200 rpm for 24 hours. Samples were retrieved and filtered. Inductively Coupled Plasma-Atomic Emmision Spectroscopy (ICP-AES) analysis of the depleted solution was performed.

**Neodymium:** 70 milligrams of fully hydrated neodymium chloride (NdCl₃*6H₂O) were dissolved in one liter of DI water, and left at the intrinsic pH. From this solution, 100 mL was added to 0.5 grams of various ion exchange media and nanoscale magnetite powder. The samples were agitated for 24 hours, and a 20 mL sample was drawn and filtered. The samples and functional groups of each media were as follows:

- BTNd 1.0 - Untreated Neodymium Chloride Solution
- BTNd 1.1 - Glucamine
- BTNd 1.2 - Sulfonic Acid
- BTNd 1.3 - N-(Carboxymethyl)- N-[(4-ethenylphenyl)methyl]glycine disodium salt
Berkeley Pit: A series of experiments was conducted in order to assess adsorption performance of magnetite and MNC in actual samples from the Berkeley Pit. The first two experiments were performed with the sample as received, the remainder after a precipitation process, as per Rosenberg [9].

- A 325 mL sample of Berkeley Pit water is placed in the shaker table adsorption apparatus. The precipitation procedure for experiments 3-6 is as follows:
- Iron was oxidized with addition of 4 mL hydrogen peroxide, and then precipitated through a pH adjustment with sodium hydroxide to pH=4.4. The precipitate was collected and the filtered supernate was utilized for the remaining experiments.
- A 1.0 gram sample of 20-30 nm diameter magnetite (Fe₃O₄) particles, or MNC particles, is covered in approximately 30 mL ethanol and agitated on a shaker table. Following full dispersion, 100 mL of DI water is added and agitated further. The mixture is then placed under vacuum for approximately six minutes or until all off-gassing ceases. The remaining slurry is placed on a shaker table until needed.
- The entire apparatus is placed on a shaker table at 105 RPM. The Pit water and particle slurry are combined in the pipe and a timer is started. A 10 mL sample is retrieved from a point 130 mm from the top of the pipe at exactly 45, 180, and 300 seconds.
- Samples are immediately filtered through a 0.45 µm syringe filter and placed in a 20 mL scintillation vial. It appears the vast majority of particles are removed and adsorption ceases.
• The samples are analyzed via ICP-AES utilizing a geochemical standard consisting of 18 common elements found in local mine affected waters.

**Industrial Process Stream**

Four experiments were conducted with samples from an undisclosed mining process stream. The samples were rich in gold and silver, with copper as a contaminant targeted for removal. The experiments were performed on the shaker table, as in the magnet adsorption experiments, but with no magnetic field or core wires. The as received sample had a high pH of approximately 14. Two experiments were performed at high pH (1&2) and the other two after a pH reduction to approximately 3.5 with sulfuric acid (3&4). All experiments utilized coated particles from Dr. Rosenberg’s laboratory, batch REL5. Experiments were conducted with the same method as the Berkeley Pit experiments, except for the precipitation procedure and ICP-AES method.

**3.4. Electrowinning**

A novel annular electrowinning cell was investigated in order to assess the potential for an electrochemical recovery of metals within the final stages of the process. These cells, developed by EMEW Technologies, have been purported to operate effectively at lower solution tenors than traditional electrowinning methods [61]. In contrast to conventional methods, in these annular cells the solution flows tangentially through a cylindrical cathode, as shown in Figure 26. The annular electrowinning cell presents many advantages, most based upon improved mass transfer [62] [63]. Improved mass transfer results in increased capacity, reduced footprint, increased selectivity, and plating from lower concentrations. In
the context of this research, an electrowinning technology capable of direct integration into a high flow, low metal concentration flow is advantageous.

3.4.1. Apparatus and Method

Figure 26: Conventional electrowinning on the left, EMEW annular, tangential flow electrowinning on the right. [91]

Figure 27: Laboratory scale EMEW electrowinning cell
The complete apparatus, pictured in Figure 27, consists of a Little Giant 110 volt 1/30 hp impeller pump with flow meter, a hand operated priming pump, a heated ceramic cask, the EMEW laboratory-scale annular electrowinning cell, a GW Instek SPS 1230 DC power supply, and the associated acid resistant tubing and valves. The method was as follows:

- The appropriate starter sheet is inserted into the cell, typically stainless steel for copper [64] and aluminum for zinc [65]. The anode is replaced and all fittings are tightened to specification.
- Five liters of DI water is added to the cask along with the desired quantity of salt. For copper, reagent grade CuSO₄·5H₂O, and for zinc, reagent grade ZnSO₄·7H₂O. Heating is initiated and allowed to equilibrate.
- Once the desired temperature is achieved and the salts dissolved, the pump is primed utilizing the hand pump. The pump is initiated and the flow is adjusted via the main valve, typically to eight liters per minute. The pump was run for a minimum of three minutes as to ensure complete mixing of the solution.
- A sample is drawn from the cask in order to establish initial concentrations. All samples are 15 mL, are immediately filtered through a 0.45 µm syringe filter, and are placed in a 20 mL scintillation vial with the appropriate label.
- The electrical leads are connected, positive to the titanium oxide anode and negative to the body of the cell, typically to a bolt at the base. Dielectric grease is applied to ensure connectivity.
- The power source is energized in continuous voltage mode and set to the desired parameters, typically 2.5 volts for copper and 4.5 volts for zinc.
- Samples are drawn from the port at the base of the cell every hour. A flush of 20 mL is drawn and discarded followed by the actual sample of 15 mL. Temperature and pH tests are performed on the solution in the cask. Data were recorded hourly, including temperature, pH, flow rate, current, and voltage.
- Solution samples are analyzed by ICP-AES for copper or zinc concentration and the resulting metallic cathode is dried and weighed.
3.5. Pilot-Scale Reactor Experiments

3.5.1. Helical Reactor

3.5.1.1. Apparatus

The design and construction of a third generation reactor was initiated in November 2015. The decision was made to scale-up the reactor from previous iterations in order to demonstrate scalability and industrial application. A two-inch inner diameter pipeline reactor was chosen. This route poses significant challenges, especially with magnetic collection, as the magnetic field strength decreases proportional to the cube of the radius, as given by the Biot-Savart equation.

The chemistry of the Berkeley Pit water was considered as the design basis of the reactor. Concentrations of various metal ions are well known, and sampling and characterization is ongoing. Copper, zinc, and manganese were chosen as the initial target ions because of their abundance, economic value, and potential threat to the environment. Other parameters were gleaned from Montana Bureau of Mines and Geology data dated June 14, 2012: 790 ft below the surface temperature, pH, and ORP were measured at 6.0˚C, 2.60, and 680 mV, respectively. Extensive sampling and analysis was completed by Dr. Alysia Cox and her students, characterizing local mine affected waters [26]. The selection of target metals and other conditions were substantiated by these analyses.

The limited timeframe of the project necessitated concurrent development of the nanoparticles along with the design of the reactor. Without access to, or detailed characterization of, the nanocomposite ion exchange media, many assumptions were necessary. It was believed the finished nanocomposite would be roughly spherical with a diameter of approximately 200
nm. It was assumed these particles would behave as colloidal matter, suspended in the solution with Brownian motion dominating the movement. This assumption later proved to be erroneous.

The 3\textsuperscript{rd} generation helical experimental reactor consists of a 12.26-meter-long helical tube wrapped around a steel support structure (Figure 28). The tube is 2 inch or 5.08 cm inside diameter polyvinyl chloride (PVC) pipe. The total volume of the reactor is approximately 99.5 liters. The total elevation head is approximately 1.5 meters.

![Figure 28: 3rd generation reactor](image)

The final leg of the reactor is divided into two paths, each with a magnetic collection module, allowing continuous flow. At any given moment, one side is in particle collection mode.
while the other is being flushed, sending particles to the strip and regeneration circuit, and ultimately to be reused. The paths are determined by operation of four pressure operated, solenoid controlled valves.

**Experimental Method**

A 40 liter reservoir is positioned above the system and provides the bulk solution. A given amount of copper (II) sulfate pentahydrate salts are massed and allowed to solubilize in a 2-liter flask of deionized water. The solution is then added to the reservoir and thoroughly mixed with an impeller mixer. The solution is fed to a 1/3HP Dayton Vane pump, providing a variable flow from 0 to 23 liters per minute. The flow is routed through a Micro Motion Inc. Coriolis meter, which continuously measures solution temperature, density, and instantaneous and cumulative flow. Near the beginning of the helix, a slurry consisting of the nanoparticles and deionized water is injected into the flow via a 0.1 hp Cole Parmer peristaltic pump. A static PVC inline pipe mixer with 12 blades and a length of 0.89 meters is incorporated 3.6 meters downstream. The final leg of the reactor is divided into two paths, with each path leading to an electromagnetic capture module. A solenoid valve allows the flow to be diverted from one side to the other. In practice, one side will operate in magnetic collection mode while the other is de-energized and the concentrated nanoparticle slurry is collected. This scheme allows for continuous operation. Samples of 10 mL aliquots are withdrawn at given time intervals from the effluent of the system into 30 mL syringes. The sample is then immediately filtered via Whatman Puradisc 25 PVDF membrane syringe filters directly into 20 mL scintillation vials for storage until analysis.
Automation and Data Logging

Montana Tech Electrical Engineering student, Thad Haines, was enlisted to assist with the development of an automation and data logging system. Initial goals of timed automated cycles, logging temperature data of each magnet within ±1 °C and the input pH every second. An Orion Star A214 pH (OSpH) meter had the ability to communicate readings via the serial communication standard RS-232.

A Raspberry Pi micro controller (RPI) was to act as the master controller and data logger for the project. The RPI has a very large user base and is Python friendly, and an open source code was written as an alternative to Labview. Licensing fees could be avoided, serial communication could be used to read pH data from the pre-existing meter, and a custom graphical user interface (GUI) could be designed for users to easily set mode times and view real-time system data.

Figure 29: Schematic of complete control system
The instrumentation diagram in Figure 29 shows the schematic of the complete control system. The shaded yellow region indicates what was improved upon or added to the original system which includes the RPI and touchscreen, a customized Printed Circuit Board (PCB), an updated manual control panel, a relay solution, and data acquisition for temperature and pH.

The processor behind the automation and data collection of the system is a Raspberry Pi 3 (Figure 30). Features include the number of available universal serial bus (USB) ports, onboard Wi-Fi, integrated circuit (I2C) capability, and a DSI connector that enabled use of a 7” touchscreen.

![Figure 30: Control system micro-processor](image)

One of the USB ports is dedicated to communicating to the OSpH meter through a USB-RS232 adapter while another is reserved for a thumb drive that contains the custom code and stores the created data logs. The I2C bus is used for communication to 3 general purpose input output (GPIO) expanders and a 12 bit analog to digital converter (ADC). Two eight channel expanders serve as digital output banks used to trigger to each device’s associated relay while the 3rd expander is 16 channels and functions as a digital in to monitor system status. The monitored point of this 3rd expander is after the manual control and thus reflects the actual voltage level
seen by the relay. Each relay was allotted 20 mA for proper operation and as such, required more than one expander could provide.

The ADC on the I2C bus collects voltages from two thermistors placed inside the fluid flow near each magnet. This voltage level is converted to a useful temperature through a coded lookup table and a linear approximation process. Since the thermistors are to be used in an enclosed space, testing of the thermistors was carried out prior to installation.

The touchscreen is oriented vertically and the initial interface is very similar to one that may be found on any modern PC. A 5 VDC, 2.4A power supply is used for powering the RPI and touchscreen as well as all manual control panel LEDs and GPIO expanders.

The code involved in the project, which can be found in Appendix B, utilized built-in Python 3.4 libraries for most functionality, an open source adafruit library for easier analog to digital conversion, and PySide Qt bindings for GUI elements. This combination of software was chosen so that the finished project would adhere to the GNU Lesser General Public License Guidelines (LGPL). This precaution essentially means no licensing fees were required and, if desired, the code could be sold or incorporated into other proprietary projects as long as the LGPL code was made available to any end users.

The completed GUI is shown in Figure 31. As shown on the left side of the figure, mode times are selected via dropdown menus. The right side of the figure shows a typical Run Mode screen where system time, system status, device status, pH, and temperatures update every second while mode times updates every 0.05 second. A PCB was designed for easier connectivity between the Raspberry Pi, manual control panel and thermistors (figure 32).
Figure 31: Graphical user interface

Figure 32: Printed circuit board design (left) and finished product (right)
Another feature added to the PCB was a set of I2C Level Shifters, which enabled the GPIO expanders and ADC to operate at 5 V instead of the default 3.3 V. This difference meant the relays selected could have a higher threshold voltage and the ADC would have a larger usable range.

The control panel faceplate incorporates switches for each valve, pump, and magnet, with LED lights indicating on, off, or automatic run. The finished faceplate with switches and touchscreen control panel, is shown in Figure 33.

![Control system face plate](image)

**Figure 33: Control system face plate**

### 3.5.2. Vertical Reactor

In December 2016, the design and commissioning of a vertical fourth generation reactor was initiated. Challenges encountered with agglomeration and settling of particles in the 3rd generation helical reactor prompted a complete redesign of the reactor. It was hypothesized that if the effects of gravity on the particles could be negated or incorporated, research could continue regardless of settling or dispersion characteristics. If proven successful, this approach could
eliminate a potential pitfall for commercial implementation, as well. A vertical pipeline reactor was devised with operating parameters similar to that of the previous iteration.

3.5.2.1. Apparatus

The fourth generation reactor consists of a constant head, gravity fed vertical column. The reactor is approximately 5 meters tall with a total volume of 120 liters. Solution flow rates of 1 to 20 liters per minute can be examined. Specialized static mixing components described in the next section are incorporated in the column. It will operate in the same manner described regarding the third generation reactor, with a second column and collection module eventually installed. In practice, one side will operate in magnetic collection mode while the other is de-energized and the concentrated nanoparticle slurry is collected. This scheme allows for continuous operation (Figure 34). This schematic details the magnetic collection modules in the two cycles of the continuous flow process; the red circles signify a closed valve, and green open. The blue line signifies the flow path, with a suspended path denoted with a dotted line.

Figure 34: Schematic of collection modes
The automation and data logging system will eventually be dedicated to this system, with only minor alteration necessary. Special full-port, electronically operated valves were incorporated in order to control and divert flow. These valves have an oversized ball so there is no reduction to flow, nor voids where particles may collect. The complete reactor is pictured in Figure 35.

Figure 35: Vertical reactor
Advancements were achieved with the magnetic collection module, as well. In this iteration, a 6 inch PVC wye serves as the module, with the electromagnet positioned near the top at a 45° angle, as shown in Figure 36. When energized, the flow of depleted solution proceeds over a weir and out the other end of the wye. In collection mode, the magnet is de-energized and the concentrate is collected at the bottom. The module was fabricated with a special clamping system allowing easy inspection and cleanout. The design of the clamps is detailed in Appendix A. The wye collection module is shown in Figure 37. The vertical reactor was designed to be modular, and was constructed on a mobile stand capable of accommodating the two columns required for continuous flow.

![Figure 36: Illustration of flow paths within collection module](image_url)
3.5.2.2. Mixing

Two aspects of mixing have been examined in detail, in the context of this research and the laboratory scale experiments:

1. Mixing of the metal bearing solution with the particle slurry
2. Mixing of loaded particles and solution with uncontaminated water within the column and collection module at the initiation of experiments

Mixing of the metal bearing solution with the particle slurry

The 3rd generation reactor utilized an off-the-shelf static mixer, 0.89 meters long with 12 blades. For the 4th generation reactor, a more modular and expandable mixing alternative was desired. A suitable product could not be readily found, so a new in-line mixer configuration was devised. In collaboration with The Center for Advanced Materials Processing (CAMP), a novel
modular mixing component prototype was designed and manufactured. After several iterations, the following design was selected (Figure 38):

Counter-inclined blades are paired with a ball-and-socket connection scheme. The slot and nipple ensure consistent alignment. This design allows for a wide range of applications. The component is modular and easily scalable, allowing for implementation in any pipe size and with as much mixing as is necessary. The connection allows for an arcing alignment, facilitating installation in a helical pipeline. Quantification of the mixing efficacy will be discussed in the subsequent recommended future work section.

**Mixing with uncontaminated water within the column and collection module at the initiation of experiments**

In order to accurately characterize the startup of the process, mixing experiments would be conducted to establish a baseline of dilution. The utilization of batch experiments in order to
model continuous flow processes presents some challenges. Limited quantities of MNCs necessitated short experiments in which the reactor is started full of water. The dynamics of mixing of the copper sulfate solution with the water in the reactor was modeled at various flows.

3.5.2.3. Experimental Method

The method for experiments with the 4th generation reactor is summarized in this section, though some variation was encountered such as use of bare magnetite particles in some experiments. All experiments were conducted at room temperature (21°C average) and at ambient pressure. Copper (II) sulfate pentahydrate salts were procured from Cole Palmer and were 99% pure. All analysis were performed by ICP-AES or spectrophotometry, as detailed in the analytical section.

- The reservoir is filled to the previously established starting mark with a copper sulfate solution calculated to produce the desired concentration. The solution is thoroughly stirred with a handheld impeller. A sample of 15 mL is retrieved, filtered, and placed in a scintillation vile for analysis. The column is filled with water and the top valve is opened.
- The desired mass of MNCs is dispersed within 50 mL of ethanol and 400 mL of DI water, as detailed in the dispersion method previously discussed.
- A 900 mL slurry is created by combining the dispersed MNCs with the appropriate volume of DI water. The hopper is prepared for the slurry by backflushing the contents of the column to the previously established low mark and engaging the stirrer at 70 RPM. The slurry is then added.
- Cumulative flow is read and recorded from the MicroMotion coriolis meter. The pH of the reservoir is measured, via an Orion Star A214 pH meter, and is recorded.
The experiment is initiated by opening the main valve and engaging the slurry peristaltic pump. The time is recorded. The effluent flow is directed through the scavenger magnet into the effluent vessel.

The electromagnetic coil is energized as soon as flow has been established. The power supply, a BK precision 1902 DC Switching power supply, is set to the desired amperage in continuous current mode. The initial current and voltage are recorded. It is essential the magnet not be energized without flow.

At predetermined intervals, samples are collected from the effluent just downstream of the scavenger magnet. Samples are approximately 15 mL retrieved by syringe, immediately filtered, and placed in a scintillation vile for analysis.

Timing of various events are recorded, i.e. first particles to magnet, last particles to magnet, and hopper empty.

Once all MNCs have passed through the collection module, time is recorded and main valve is closed. The magnet is de-energized and after one minute the module is drained into the concentrate vessel. Samples are collected from the effluent and concentrate vessels, and pH is measured in each.

The scavenger magnet is disassembled and renegade particles are dried for quantification.

The particles in the concentrate are collected with permanent magnets and prepared for stripping.

The seven baseline mixing experiments were conducted as described above, with the exception that no particles or slurry were added. These experiments were conducted over a range of flows and copper concentrations similar to those in actual experiments. The effluent solution was sampled at predetermined time intervals and analyzed by ICP-AES or spectrophotometry.

Twenty-two experiments were conducted in the vertical reactor, as described in the preceding method. Flows ranged from 1.7 to 3.5 LPM. Initial concentrations ranged from 40 to 540 mg/L of copper. Three batches of MNCs were utilized, all with PAA functionality. One experiment was conducted with actual mine water, a sample from the Parrot Tailings complex.
Seven experiments in series 30 examine adsorption within the vertical column before reaching the magnetic collection module. A sample port was installed just above the collection module for this purpose. These experiments have a low flow and low copper concentration, and utilize raw magnetite as the adsorption media. Findings in earlier experiments were the impetus for this study; results showed lower than expected loading. Two possible scenarios were considered to possibly be inhibiting adsorption: insufficient residence time and/or competing ions. Although the majority of loading in bench-scale experiments was shown to occur within the first minute or two, a longer residence time may be required in the reactor. An expanded chamber was added to the top of the reactor, effectively doubling the residence time. The possibility of competing ions from the tap water used was considered, and experiments were conducted utilizing reverse osmosis treated water.

3.6. Stripping

A protocol for the stripping and regeneration of the nanocomposite particles has been established. The citric acid utilized by the team at University of Montana proved problematic in the electrowinning cell, so alternatives were sought. Sulfuric acid was found to be suitable. The following protocol has shown to strip the metal ions effectively with minimal leaching in subsequent wash cycles.

- Prepare a 500 mL solution of sulfuric acid and DI water, adjusted to a pH of 2.
- Add dewatered slurry of loaded particles to solution. Agitate with wrist action for 3.5 minutes. Allow to settle for 3.5 minutes.
- Apply permanent magnet array to side of beaker, near spout. Pour supernatant solution into receptacle. Remove as much liquid as possible without loss of particles.
- Add DI water to particles to total 500 mL. Agitate for 3.5 minutes and settle for 3.5 minutes. Apply permanent magnet array to side of beaker, near spout. Pour wash water
into receptacle. Remove as much liquid as is possible without loss of particles. Repeat wash cycle twice.

- Prepare a 500 mL solution of ammonium hydroxide and DI water, adjusted to a pH of 11.
- Add dewatered slurry of stripped particles to solution. Agitate with wrist action for 3.5 minutes. Allow to settle for 3.5 minutes.
- Apply permanent magnet array to side of beaker, near spout. Pour supernate into receptacle. Remove as much liquid as is possible without loss of particles.
- Add DI water to particles to 500 mL. Agitate for 3.5 minutes and settle for 3.5 minutes. Apply permanent magnet array to side of beaker, near spout. Pour wash water into receptacle. Remove as much liquid as is possible without loss of particles. Repeat wash cycle twice.

An additional experiment was conducted in order to assess the possibility of stripping copper from the raw magnetite particles via pH adjustment. Ten grams of particles were allowed to completely load in a strong solution for 48 hours. The particles were separated via an external permanent magnet and the supernate decanted. The loaded particles, with a minimum of remaining solution, was introduced to 500 mL of a sulfuric acid solution, pH 1.35. The mixture was agitated for 3 minutes, then allowed to settle for three more, and then a sample was drawn and filtered. The analysis showed a concentration of 321 ppm, a load of approximately 160 mg. This result suggests a strip of 0.25 mmole/gram of magnetite. Future experiments will be attempted to confirm and/or improve on the result along with assessing regeneration and multiple cycles.
4. Results and Discussion

4.1. Initial Scoping and Basis

4.1.1. Wastewater Characterization

In total, LEGEND secured 42 samples, which have been analytically characterized for metal content, pH, and other relevant parameters. Nine flooded underground mine complexes were sampled: Anselmo, Kelley, Steward, Ophir, Travona, Emma, Pilot Butte, Orphan Boy, and Orphan Girl. Additionally, the Horseshoe Bend water treatment plant and three wells, including wells tapping the high-copper Parrot tailings were sampled. The results of the wastewater sampling and analysis efforts validate the selection of copper, manganese, and zinc as principal target metals in laboratory and bench-scale evaluations as LEGEND detected significant concentrations of these metals in most of the samples. Large-volume samples for confirmatory testing in the pipeline reactor have been secured from the Berkeley Pit, Travona, Ophir, and Kelley mines, and the Parrot Tailings. Example data from three samples are shown in Figure 39.

Figure 39: Metal concentrations and pH of three mine-affected water samples [26]
These data are representative of the findings. As can be seen, The Berkeley Pit and other mine samples all contain elevated levels of copper, zinc, and manganese, to varying degrees. The pH values measured all fall within the operating range of the process. A host of other metals are present and may present opportunities in future work.

Collectively, these data were used to form the basis of the chemistry targeted by this research. Process parameters were tailored to reflect local mine water and the associated characteristics. The target metals were limited to copper, zinc, and manganese, though some other species of interest were examined. Surrogate solutions were utilized, prepared from reagent grade chemicals. The majority of the experiments utilized a copper sulfate solution at concentrations from 100 to 500 mg/L. Some real mine waters, as selected based on the work of Dr. Alysia Cox and LEGEND, were sampled and utilized in the system. Flow rates were limited to 2-8 LPM.

4.1.2. Fundamental Aqueous Processing Data and Process Models

Kinetic adsorption experiments were conducted to provide the theoretical framework for a detailed process model. The availability of reliable computational process models is invaluable to commercial process design and scale-up efforts. In addition to the obvious design considerations, models that are able to accurately predict system performance based on the selection of input parameters can be used to guide operating decisions. Operating data generated during this study are used to refine computational models that simulate the behavior of the magnetically susceptible nanocomposite materials within the continuous flow reactor system.

Kinetic experiments were performed with the PAA modified particles. The rate of metal capture is an important parameter in the design and operation of the reactor as it will determine minimum residence times. These experiments were performed under two initial concentrations,
1500 PPM and 150 PPM, with 100 mg of particles. The depleted solution was analyzed via Atomic Absorption Spectroscopy, providing the results depicted in Figures 40 and 41:

Figure 40: Rate of capture of Cu ions from a 150 PPM solution [24]

Figure 41: Rate of capture of Cu ions from a 1500PPM solution [24]
As can be seen in the 150 PPM copper solution experiment, the majority of the loading takes place within the first minute. This concentration is more typical of potential waste streams, and the rapid loading bodes well for the proposed process. These results were compared to that of previously prepared micro-scale particles with similar functionalization, and the nanoscale particles were found to be ten times faster [66]. This finding reinforced the hypothesis that the smaller particles with greater surface area per unit mass will outperform the larger particles, kinetically.

These kinetic data were also used to establish equilibrium models and adsorption isotherms. A strong correlation to the Langmuir isotherm was established, using the following equation:

\[
\frac{C_e}{q_e} = \frac{1}{bq_{max}} + \frac{C_e}{q_{max}}
\]

(18)

where \(C_e\) is the equilibrium solute phase concentration in aqueous phase (mg copper/L water), \(q_e\) is the equilibrium adsorption capacity (mg copper/g particles), \(q_{max}\) is the maximum
adsorption capacity (mg copper/g particles), and \( b \) is a constant determined by plotting \( \frac{C_e}{q_e} \) versus \( C_e \), as shown in Figures 42 and 43.

**Figure 42: Langmuir linearization of kinetic data at 1500 ppm**

**Figure 43: Langmuir linearization of kinetic data at 150 ppm**
The correlation with the Langmuir model is strong ($R^2 > 0.99$), indicating a true Langmuir adsorption model is applicable. This model is a typical indication of monolayer adsorption and true ion exchange.

Examination of scalability and the dimensionless numbers described in section 2.6 led to a theoretical model of magnetic separation based upon magnetic field strength, flow rate, and particle size. In the simplest terms, the magnetic force must be greater than or equal to the hydrodynamic drag force. Other forces at play, such as gravitational and buoyant, are negligible when applied to particles in the size range involved in this research.

The hydrodynamic drag force is given by Stoke’s law [67]:

$$F_d = 6\pi r_p \mu v$$  \hspace{1cm} (19)

Where $F_d$ is the drag force, $r_p$ is the particle radius, $\mu$ is the viscosity, and $v$ is the fluid velocity. The applicability of Equation 19 requires specific flow conditions. These conditions may be determined with the dimensionless Reynolds number (section 2.2) across various scales. In this case with $L$, the characteristic length, as the particle radius, a Reynolds number of 0.05 or less is required. Consider typical conditions within the vertical reactor experiments where $L=200$ nm, $v=0.0247$ m/s, and the typical properties of water are assumed. In this case, the Reynolds number is 0.0055, well within the limitations of Stoke’s Law. This constraint is applicable over all scale-up situations.

In order to quantify the magnetic force over various scales, a modified form of the Peclet number is utilize [68] $d$, as given by:

$$P_e = \frac{r_p \cdot F_m}{KT}$$  \hspace{1cm} (20)
Where $F_m$ is the magnetic force, $K$ is Boltzman’s constant, and $T$ is the absolute temperature. This variant of the Peclet number indicates that the magnetic force will dominate when $Pe > 1$. This model does not consider the fluid drag, only the Brownian motion, and can be used to establish a lower limit of magnetic capture feasibility.

As discussed in section 2.2 these dimensionless numbers will be essential for scale-up design. Because they are ratios of identical units, their qualities are preserved over a range of scale and conditions, and similitude is maintained. Experience gained in comparing these numbers to empirical findings will help guide future modeling and design.

### 4.2. Particle Synthesis

Dr. Rosenberg and his team at The University of Montana initiated the process of synthesizing the ion exchange nanoparticles in November 2015. They initially identified three methods of modifying iron magnetic nanoparticles with ligands capable of capturing metal ions:

**Method 1:** Beginning with commercially available magnetite ($\text{Fe}_3\text{O}_4$) nanoparticles (20-30 nm diameter), the surface is treated with aminopropyltrimethoxysilane (APTMS) and then reacted with Ethylenediaminetetraacetic acid (EDTA) in pyridine. This method produced particles that were easily manipulated with a magnet and dynamic light scattering measurements suggested diameters in the 1000 nm range. The loading capacities were found to be lower than those reported in literature.

**Method 2:** Co-precipitation of magnetite from ferrous and ferric salts can produce nanoparticles with diameters of approximately 10 nm. The particles are then treated with silicic acid and then APTMS to produce a functionalized surface. Loading capacities of 33mg/gm were found for copper.
Method 3: A mixture of tetraethoxysilane (TEOS) and APTES in a 4:1 ratio is used to coat magnetite particles. The particles can be co-precipitated or introduced. Capacities were similar to Method 2 at 38 mg/gm.

The next phase of experimentation examined the use of polyallylamine (PAA) as the metal capturing reagent instead of APTMS. Two methods were explored, one utilized silicic acid and the other TEOS. Various reagent ratios were investigated in order to optimize loading capacities. The two methods are illustrated in Figure 44:

Figure 44: Diagram of two pathways to conversion of iron oxide cores to polymer modified nanoparticles [69]
It was found that the two methods resulted in similar copper loading capacities (1.2 mmole/g). Scanning Electron Microscopy (SEM) images show that the TEOS method gives a thicker silica coating, as shown in Figure 45. Energy Dispersive X-ray (EDX) analysis performed by the author confirmed these findings, with the TEOS prepared particles presenting with 38-42% silica and the silicic acid prepared particles with 12-32% silica. Based on these results it was decided to focus on the TEOS method.

![Figure 45: SEM image of PAA treated nanoparticles [66]](image)

Comparisons of PAA and its branched analog, poly(ethylenemine) (PEI) were explored. PAA is a straight chain polyamine containing only primary amines. It has been covalently linked to the silica shell. PEI, on the other hand is a highly branched water-soluble polymer containing primary, secondary and ternary amino groups.
PEI has been found to be more effective in some adsorption applications and is less expensive than PAA. However, loading capacities for copper were lower compared to PAA. Some possible advantages were observed. The aggregation phenomenon observed with loaded PAA is not apparent, and dispersion is more easily achieved. These characteristics could prove valuable in specific applications.

Having settled on a TEOS-PAA method of preparation, efforts turned to scale-up and optimization. Various molecular weights (MW) of PAA were investigated and the resulting copper capacities analyzed. Other parameters, such as reaction time and reagent volumes were varied and analyzed. It was found that the 60,000 MW PAA performed the best, with the highest loading capacities.

Following optimization of the preparation, stripping and regeneration procedures were explored. Initial results with copper adsorbed to TEOS-PAA prepared particles are shown in Figure 47. As can be seen, loading is not diminished in subsequent load-strip cycles until the eleventh cycle, which is more likely due to particle loss in the wash cycles.
Functionalization via PEI may prove useful in particular circumstances. While loading capacities of PEI functionalized particles have been considerably lower than that of PAA, the PEI particles perform at a lower pH (0.05-0.1 mmole/g at pH=2) and tend to stay suspended. Depending on operating conditions, these properties may be more important than loading capacities.

Batches of particles were prepared from PAA at two molecular weights (3,000 and 60,000) and then loaded with copper, stripped and regenerated four times without loss of capacity. The corresponding copper capacities are plotted as a function of cycle number in the histogram in Figure 48. This finding illustrates the capability to repeatedly strip the metal ions and then regenerate the nanocomposite IX materials for reuse in the wastewater treatment process.
4.3. Particle Characterization

Figure 49 displays three data sets, the zeta potential of both raw magnetite particles and the coated nanocomposites as a function of pH, and the size distribution of the magnetite

Figure 49: Zeta potential and size distribution of magnetite particles, and zeta potential of MNCs
particles. As was discussed, full dispersion of individual particles was never achieved, and the size distributions in the center plot bear this fact out. As can be seen, particle diameters ranging from 200 to 4500 nm were measured via dynamic light scattering, with some correlation with pH. The widest distribution was seen at pH 2-4, precisely within the primary operational range. Size measurements for the coated particles were not possible via DLS, as the upper limits were exceeded. Zeta potentials were similarly spread within the operational pH zone, suggesting inhomogeneity due to agglomeration.

In the absence of reliable DLS size data, a set of experiments was devised in order to assess the phenomenon of agglomeration as a function of ionic strength.

![Figure 50: Light absorbance of MNC particles over time](image)

Figure 50 shows the normalized light absorption over time, as a function of ionic strength. As is shown, ionic strength has a distinct effect upon agglomeration and subsequently,
settling. Stronger solutions result in more rapid settling, which is consistent with observations in the laboratory.

![XRD difractogram of magnetite powder](image)

**Figure 51: XRD difractogram of magnetite powder**

Powder XRD analysis of the magnetite was performed, both as received and after multiple experiments. XRD showed the distinct diffractogram of magnetite, as matched by the PDXL software. Red coloring observed on the surface used of particles led to a concern the magnetite was being oxidized to hematite, and magnetic properties would be altered. XRD analysis showed no sign of any crystal structure other than magnetite.
The elemental composition of both loaded and unloaded particles was investigated by SEM-EDS. A typical micrograph and spectra of an unloaded particle are shown in Figures 53 and 54. In the micrograph, individual particles are indistinguishable. EDS measurements were made both at a point and over an area of the bulk material. The EDS spectra shows K peaks of oxygen, iron, and silicon, as expected. An average of many analysis shows the approximate composition, given in Table II. If the diameter of the magnetite core is assumed to be 25 nm, the
shell thickness can be estimated using simple geometry and stoichiometry. By this method, and the findings in Table II, a shell thickness of 0.85 nm is estimated.

Table II: Elemental composition of MNC particles

<table>
<thead>
<tr>
<th>Element</th>
<th>Mass %</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>19</td>
<td>42</td>
</tr>
<tr>
<td>Silicon</td>
<td>10</td>
<td>13</td>
</tr>
<tr>
<td>Iron</td>
<td>71</td>
<td>45</td>
</tr>
</tbody>
</table>

A typical micrograph and spectra of loaded particles are shown here in Figures 54 and 55:

A similar elemental composition is presented in the spectra with the addition of copper, and a minor peak of sulfur. The elemental composition of these loaded MNC particles is given in Table III:
Table III: Elemental composition of loaded MNC particles

<table>
<thead>
<tr>
<th>Element</th>
<th>Mass %</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
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</tr>
<tr>
<td>Silicon</td>
<td>5</td>
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<td>Iron</td>
<td>67</td>
<td>45</td>
</tr>
<tr>
<td>Copper</td>
<td>3</td>
<td></td>
</tr>
</tbody>
</table>

4.4. Dispersion

The dispersion method, defined previously, produced satisfactory results. It was found that individual particles were not dispersed; however, the maximum achievable dispersion was observed with this technique. At no point, and in no circumstance, was a true colloidal suspension achieved, either with the coated particles or the raw magnetite. This observation is consistent with the particle characterization findings, particularly the average diameters found through dynamic light scattering analysis. These analyses showed diameters on the order of one μm, suggesting agglomeration and subsequent settling. Settling velocity experiments, described
previously, showed an average settling velocity of $1.3 \times 10^{-4}$ m/s, however a wide distribution was observed with some agglomerates settling much faster and some particles remaining completely suspended.

The Transmission Electron Microscopy (TEM) image in Figure 56 shows an aggregation of MNCs that appear to be a reaction limited cluster-cluster aggregation [53]. The aggregates of particles appear to be typical fractal arrangement. It should be noted, the aggregation seen here may be an artifact arising from the preparation of the sample for microscopy. The amount of aggregation of the particles in their dispersed state and the amount seen in an electron micrograph of a dried sample may differ greatly. These considerations, along with the variability seen in other techniques, makes determining the actual dimensions, densities, and surface areas challenging. Many of the models in this work have approximated the particles as spheres,
however, it is unlikely the individual particles are spherical, let alone the aggregations. A more
detailed examination of the aggregates could improve aspects of the modeling, such as settling
behaviors based upon density.

4.5. Magnetic capture

Testing of the fabricated coils showed a resistance of 5.5 Ohm, and magnetic flux of 1.57
KG without core material. Measurements were taken both dry and submerged with identical
results. The gauss meter utilized did not have the resolution to examine high gradient fields
induced about the core wires.

Early experiments were conducted with various particles in the development stage. Coprecipitated particles with magnetite cores of approximately 10 nm average diameter were shown to have unsatisfactory magnetic susceptibility. The majority of the particles passed through the collection module without impediment at all flow rates investigated. Particles with various coatings exhibited similar behavior. The bulk of experimentation was conducted with uncoated 20-30 nm diameter magnetite particles, with the assumption that thin coatings would not affect magnetic susceptibility significantly. Confirmatory experiments were conducted with MNC particles.
Flows up to 8.1 LPM with particle masses up to 80 grams achieve the target benchmark of 98% collection efficiency. The availability of only limited quantities of coated particles restricted extensive study. However, multiple experiments suggested a close correlation between collection efficiencies of raw and coated particles.

The curves fit to these data confirm two theories brought forth in the theoretical considerations section. The declining collection efficiencies experienced with greater mass of particles corresponds to excess particle buildup on the core wires. At some level of buildup, as a function of fluid velocity, the magnetophoretic force is exceeded by the fluid drag force and particles are lost into the flow. As expected, these curves slope more dramatically in high flow regimes.

Figure 57: Magnetic particle collection efficiencies
The reduced collection efficiencies experienced at lower mass of particles is explained by cooperative magnetophoresis. Cooperative magnetophoresis is the phenomenon where aggregates of particles are more susceptible to a magnetic field than individual particles. As particles, or the cores of MNCs, are magnetized, they tend to agglomerate with other particles that are sufficiently close. This phenomenon is illustrated in Figure 58:

![Illustration of cooperative magnetophoresis](image)

**Figure 58: Illustration of cooperative magnetophoresis**

Magnet cooling by the metal and water solutions proved effective. Even at the lowest flow rate, amperage was maintained and performance continued. Periodic testing of the resistivity of the coil ensured no degradation had occurred. A typical plot of the temperature monitored on the surface of one of the electromagnetic coils is shown in Figure 59:

![Plot of coil temperature over time](image)

**Figure 59: Plot of coil temperature over time**
Energy requirements of the electromagnet were estimated. As it was operated in experiments detailed in this work, at 8 amps and 54 volts, the magnets would consume 432 watts. For comparison, this wattage is roughly equal to that of a home television. Using a sample cost of $0.15 per kilowatt-hour, 24 hours/day, this energy consumption equates to $568/year.

4.6. Bench Scale Experiments

4.6.1. Adsorption within a magnetic field

In total, twenty-six experiments were performed to examine adsorption within a magnetic field. A distinct difference in the adsorption rates with and without the magnetic field was observed, with slower adsorption found when the field is present. Furthermore, it was found that nano-scale magnetite particles perform well in these experiments, removing over 90% in the first 45 seconds, on average. Adsorption kinetics of this time scale are significantly more rapid than macro-scale adsorbents.

The mechanisms of magnetic field effects were initially not entirely clear. Two possible scenarios may be at work: the field is affecting the surface charge, and/or the agglomeration of the particles around the core material is limiting the available surface area. Initial scoping experiments showed the field alone did not deter adsorption. The application and release of the magnetic field had little effect on adsorption performance as would be expected if the field was affecting surface energy. These findings suggested that magnetic agglomeration was the underlying cause of retarded adsorption kinetics. A method to determine the actual mechanisms was explored in the following experiments.
Adsorption experiments in which a core of 200 wires (core I) and a core of 20 wires (core II) showed a distinct difference in adsorption efficiency. The average efficiencies of each core at 420 seconds are shown in Figure 60.

Core I has consistently higher efficiency. Over a series of six experiments a clear difference in removal efficiency was evident. This disparity was most pronounced at the seven-minute sample interval, with a consistent difference of around 8% removal efficiency. This phenomenon can be explained by a reduced effective surface area as particles build up on the wires in the presence of high gradient magnetic fields. In a given volume of solution, and with a given mass of particles, the layer will be thicker with fewer wires to build up upon. A thicker
layer will have a lower specific surface area. This effect can be modeled using the geometry of
the scenario, demonstrated in the simplified illustration in Figure 61.

In this illustration, the red denotes available surface area on the same number of particles
on one wire on the left, and two wires on the right. If it is assumed the particles are spherical and
assemble in a face centered cubic arrangement on the wires, the formula for the specific surface
area of a packed bed can be utilized, as in Equation 21 [70]:

$$F \_B = \frac{\pi a^2}{\pi (d^2/6)} = \frac{6}{d}$$

where $S_B$ is the specific surface area ($m^2/m^3$ or $m^{-1}$) and $d$ is the diameter (m). The formula
reduces to a simplified six divided by the diameter. If it is further assumed that particle build-up
approximates a cylinder around the core wire within the zone of high gradient magnetic fields,
the total effective surface area may be approximated by Equation 22.

$$S \_T = S_B V + S_S$$
where $S_T$ is the total effective surface area, $V$ is the volume of the cylinder and cone ends, and $S_S$ is the surface area of the cylinder and cone ends. However, the total effective surface area is not representative of the kinetic reality. As particles build up around the core wires (Figure 62), the resulting packed volume becomes impenetrable. If spherical particles of a diameter of 1 µm are assumed, the flow paths are only 215 nm², seriously limiting the diffusion of the solution within the bed. Particles in the 20-30 nm diameter range will completely deter flow. Ample pathways between the cylindrical packed volumes allow for short-circuiting.

![Conceptual model of particle buildup on a core wire](image)

**Figure 62: Conceptual model of particle buildup on a core wire**

In this case of limited flow within the particle build-up, the surface area of the cylinder and cone ends dominates the effective surface area. Take, for example, the approximately 2 cm³ of particles utilized in these experiments with cores I and II. When this volume is distributed over the 200 wires in core I, the effective surface area is 4.45 times greater than that of core II
with its 20 wires. The results of the experiments with each core suggest this increased effective
surface area plays an important role in adsorption efficiency.

Twenty-six experiments were completed. The first eight were conducted with an initial
concentration of 8ppm and the last eighteen with an initial concentration of 16ppm. The rapid
adsorption continues with the higher concentration, and the lesser adsorption in the presence of
the magnetic field continues, as well. It is proposed that the magnetic field itself has little to no
effect on the adsorption, however, the agglomeration caused by the field, around the core wires,
explains the reduced adsorption capacity and retarded kinetics.

4.6.2. Bottle and Shaker Table Tests

Magnetite and MNC copper bottle tests

Early experiments sought to establish total loading capacities of magnetic nano-composites
(MNC) as well as raw magnetite nano-particles by agitating particles within a copper (II) sulfate
solution for 24 hours. ICP-AES analysis of the depleted solution was performed, and the results
are given in Table IV. The coated particles outperformed the raw magnetite by a significant
margin. Although these were some of the earliest PAA functionalized particles, the performance
was as predicted by U of M researchers at 0.71 mmole/g.
Table IV: General bottle test results

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<tr>
<th></th>
<th>Copper Concentration (mg/L)</th>
<th>Removal Efficiency (%)</th>
<th>Loading (mmole copper/g media)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Challenge Solution</td>
<td>1220</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Raw magnetite NP</td>
<td>914</td>
<td>25</td>
<td>0.30</td>
</tr>
<tr>
<td>Dispersed magnetite</td>
<td>899</td>
<td>26</td>
<td>0.31</td>
</tr>
<tr>
<td>MNC</td>
<td>481</td>
<td>61</td>
<td>0.71</td>
</tr>
</tbody>
</table>

**Neodymium Bottle Tests**

Bottle tests were performed with a neodymium solution in order to assess the adsorption performance of magnetite and various commercially available ion exchange media. These comparisons were made as an initial scoping experiment to inform future research into neodymium removal from mine affected waters. The results are given in Table V. The magnetite, as well as two of the ion exchange media performed well, removing greater than 99% of the neodymium in solution.
Berkeley Pit Shaker Table Experiments

Six experiments were conducted with the Berkeley Pit water, two as received and the remaining four after a precipitation protocol. The experiments were performed on the shaker table, as in the magnetic adsorption experiments, but with no magnetic field or core wires. The first and third utilized coated particles from Dr. Rosenberg’s lab, the second with raw magnetite. None of these experiments showed significant reduction in copper concentration; the concentration was reduced from around 51 ppm to 41 ppm. It was hypothesized that iron or other ions may be interfering, and a plan was devised to precipitate what gangue metals could be effectively separated. The remaining experiments, all utilizing the coated particles, presented similarly poor results.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Nd (µg/L)</th>
<th>functional group</th>
<th>Dose (g)</th>
<th>Removal %</th>
<th>Loading (mmole/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BTN-1.0</td>
<td>15600</td>
<td>Challenge Solution</td>
<td>NA</td>
<td>0.000</td>
<td>NA</td>
</tr>
<tr>
<td>BTN-1.1</td>
<td>882</td>
<td>Glucamine</td>
<td>0.5045</td>
<td>94.346</td>
<td>0.020</td>
</tr>
<tr>
<td>BTN-1.2</td>
<td>0.5</td>
<td>Sulfonic acid</td>
<td>0.5065</td>
<td>99.997</td>
<td>0.021</td>
</tr>
<tr>
<td>BTN-1.3</td>
<td>0.5</td>
<td>carboxymethyl</td>
<td>0.5053</td>
<td>99.997</td>
<td>0.021</td>
</tr>
<tr>
<td>BTN-1.4</td>
<td>7480</td>
<td>carboxylic acid</td>
<td>0.5024</td>
<td>52.051</td>
<td>0.011</td>
</tr>
<tr>
<td>BTN-1.5</td>
<td>0.5</td>
<td>magnetite NP</td>
<td>0.5333</td>
<td>99.997</td>
<td>0.020</td>
</tr>
</tbody>
</table>
Three representative experimental results are shown in Table VI, with the initial concentrations shown in blue and the depleted solution shown in grey. Adsorption occurred among all ions tested. Adsorption rates appear indiscriminate, with an average of 25% of each ion removed in experiment 6. Although no selectivity was observed, an impressive loading of 23 mmole/g of MNC was calculated. ND signifies a non-detect.

**Industrial Process Stream**

Four experiments were conducted with samples from an undisclosed mining process stream. The samples were rich in gold and silver, with copper as a contaminant targeted for removal. The experiments were performed on the shaker table, as in the magnet adsorption experiments, but with no magnetic field or core wires. The as received sample had a high pH of approximately 14. Two experiments were performed at high pH (1&2) and the other two after a pH reduction to approximately 3.5 with sulfuric acid (3&4). All experiments utilized coated particles from Dr. Rosenberg’s lab, batch REL5. Results showed low recovery at high pH, a reduction of approximately 6% of the copper concentration. At the lower pH of 3.5, usually the

<table>
<thead>
<tr>
<th>Sample</th>
<th>Al</th>
<th>B</th>
<th>Ca</th>
<th>Cd</th>
<th>Co</th>
<th>Cu</th>
<th>Fe</th>
<th>K</th>
<th>Li</th>
</tr>
</thead>
<tbody>
<tr>
<td>BP 0.0</td>
<td>352</td>
<td>2.39</td>
<td>474</td>
<td>2.20</td>
<td>1.79</td>
<td>64.4</td>
<td>1.36</td>
<td>11.2</td>
<td>0.38</td>
</tr>
<tr>
<td>BP 1.4</td>
<td>296</td>
<td>5.59</td>
<td>403</td>
<td>1.82</td>
<td>1.50</td>
<td>54.9</td>
<td>0.16</td>
<td>9.4</td>
<td>0.32</td>
</tr>
<tr>
<td>BP 3.0</td>
<td>345</td>
<td>3.97</td>
<td>465</td>
<td>2.15</td>
<td>1.76</td>
<td>63.5</td>
<td>1.15</td>
<td>11.0</td>
<td>0.36</td>
</tr>
<tr>
<td>BP 3.4</td>
<td>224</td>
<td>3.05</td>
<td>238</td>
<td>1.51</td>
<td>1.25</td>
<td>44.5</td>
<td>0.32</td>
<td>6.9</td>
<td>0.23</td>
</tr>
<tr>
<td>BP 6.0</td>
<td>157</td>
<td>5.20</td>
<td>470</td>
<td>2.16</td>
<td>1.77</td>
<td>62.9</td>
<td>ND</td>
<td>13.0</td>
<td>0.37</td>
</tr>
<tr>
<td>BP 6.4</td>
<td>112</td>
<td>3.22</td>
<td>335</td>
<td>1.60</td>
<td>1.32</td>
<td>49.3</td>
<td>ND</td>
<td>9.8</td>
<td>0.27</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mg</th>
<th>Mn</th>
<th>Na</th>
<th>Ni</th>
<th>S</th>
<th>Si</th>
<th>Sr</th>
<th>Ti</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>BP 0.0</td>
<td>659</td>
<td>282</td>
<td>83.2</td>
<td>1.36</td>
<td>2253</td>
<td>61.1</td>
<td>1.27</td>
<td>0.08</td>
<td>591</td>
</tr>
<tr>
<td>BP 1.4</td>
<td>562</td>
<td>248</td>
<td>77.8</td>
<td>1.13</td>
<td>1687</td>
<td>52.5</td>
<td>1.14</td>
<td>0.09</td>
<td>507</td>
</tr>
<tr>
<td>BP 3.0</td>
<td>647</td>
<td>277</td>
<td>84.2</td>
<td>1.33</td>
<td>2212</td>
<td>60.4</td>
<td>1.26</td>
<td>0.09</td>
<td>580</td>
</tr>
<tr>
<td>BP 3.4</td>
<td>431</td>
<td>198</td>
<td>56.8</td>
<td>0.94</td>
<td>1242</td>
<td>43.7</td>
<td>0.83</td>
<td>ND</td>
<td>413</td>
</tr>
<tr>
<td>BP 6.0</td>
<td>654</td>
<td>280</td>
<td>496</td>
<td>1.34</td>
<td>2194</td>
<td>43.9</td>
<td>1.27</td>
<td>0.09</td>
<td>584</td>
</tr>
<tr>
<td>BP 6.4</td>
<td>496</td>
<td>224</td>
<td>378</td>
<td>0.99</td>
<td>1368</td>
<td>38.1</td>
<td>1.00</td>
<td>0.07</td>
<td>452</td>
</tr>
</tbody>
</table>
ideal condition, results were poor. Not only was no copper removed, but residual copper from the particles was apparently reintroduced into the solution. The presence of cyanide complexes in the sample may explain this phenomenon.

Table VII: Industrial Process stream shaker table experimental results

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Au (PPM)</th>
<th>Ag (PPM)</th>
<th>Cu (PPM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GS 1.0</td>
<td>69.4</td>
<td>12.7</td>
<td>420</td>
</tr>
<tr>
<td>GS 2.4</td>
<td>41.9</td>
<td>6.93</td>
<td>394</td>
</tr>
<tr>
<td>GS 3.0</td>
<td>7.30</td>
<td>0.346</td>
<td>29.6</td>
</tr>
<tr>
<td>GS 4.0</td>
<td>7.13</td>
<td>0.015</td>
<td>17.1</td>
</tr>
<tr>
<td>GS 4.4</td>
<td>38.4</td>
<td>0.083</td>
<td>148</td>
</tr>
</tbody>
</table>

4.6.3. Stripping and Regeneration

A series of experiments was performed in order to assess the strip and regeneration protocol. As a measure of successful stripping of metal ions from the MNCs, the subsequent wash solutions and regeneration solutions were analyzed for residual metals, in this case copper. Early experiments showed significant quantities of copper in the wash and regeneration and adjustments were made. The molality of the sulfuric strip solution was increased as well as the time of agitation, resulting in near complete strip. By the fifth set of strip experiments the copper concentration in the regeneration supernate was non-detect (<1.52 mg/L) and remained at or below this level for the duration of experiments, twenty three in total.

As a measure of successful regeneration, loading capacities were reexamined periodically. Bottle tests confirmed successful regeneration, with loading capacities of 0.44 mmole/g after nine regeneration cycles, a reduction of less than 5%. Further experimentation could prove useful in optimizing the strip and regeneration protocol. Minimizing reagent requirements and wash volumes while maintaining performance would translate to greater system efficiencies.
An additional experiment was conducted in order to assess the possibility of stripping copper from the raw magnetite particles via pH adjustment. The particles were stripped, as detailed in the methods section, and the strip supernate was analyzed by spectrophotometry. The analysis showed a concentration of 321 ppm, a load of approximately 160 mg. This result suggests a strip of 0.25 mmole/gram of magnetite.

4.7. Helical Reactor

Initial experiments conducted with the magnetic nanoparticles in the third generation reactor immediately revealed a fatal flaw. The nanoparticles fell out of suspension upon injection and settled on the bottom of the pipeline. Some particles were entrained at increased flow rates but operation within the flowrate limitations imposed by the magnetic collection left the majority of the particles within the first meter of the pipeline.

Other lessons learned in the 3rd generation reactor were incorporated into subsequent designs. The pressure-activated diaphragm valves proved unsuitable in the given application and were replaced. Not only did these valves fail to function properly, they entrapped particles in voids within the valve body. Other points of entrapment, such as PVC joints and dead spaces at sample ports, were identified. Future designs should minimize these points and full port valves should be utilized. Whenever possible, modular attachments should be incorporated for ease of inspection and cleanout.

In order to determine how well the new automation and data collection system worked, two trials were run. The first trial was an automated system run and the second was a manually controlled run. As per project goals set earlier, each trial had to correctly record the system status, magnet temperatures, and pH data from the Orion Star meter. Correctly recorded data is
defined as accurately reflecting the current system performance in real time. The collected data from the automated run is plotted in Figure 63.

The log shows the system ran a predefined initialize mode for 15 seconds (FP101, FV201, FV203 ON), a side 1 run mode for 15 seconds (FP101, FP102, FP103, FV201, FV203, EM201 ON), followed by a side 2 run mode (FP101, FP102, FP103, FV202, FV204, EM204 ON), repeated the two run modes, and then went into standby (ALL off). This exact set of events was programmed to occur and all physically observed outputs behaved as expected. Temperature data appear realistic and is believed to be within the ±1 °C range previously observed. Recorded pH data matched what was being displayed on the physical meter during the test.
Though extensive experimentation was not performed with the helical reactor, the design has merit given particles with true colloidal stability. The compact configuration presents advantages with a reduced height and footprint.

4.8. Electrowinning

The emew® electrowinning system was procured and commissioned to demonstrate metal reduction from IX strip solutions with low dissolved metal tenors. The emew® design is well-suited for processing the low-metal tenor strip solutions produced in the pipeline reactor. Copper and zinc recovery from surrogate solutions have been demonstrated. Effective electrowinning was achieved with starting solutions that have been depleted to levels below 1 gram per liter of Cu$^{2+}$ ions (Figure 64) and coherent copper cathodes have been produced (Figure 65). A strong correlation is evident between the tenor of the solution and the mass of the recovered cathode with otherwise identical conditions; however, the technology proved capable of effective copper reduction at concentrations achievable by the overall process.
Figure 64: Low concentration electrowinning

Figure 65: Copper (left) and zinc (right) cathodes produced by electrowinning
The basic parameters found through experimentation with the EMEW cell are detailed here in Table VIII. As is shown, high current efficiencies were observed, comparable to conventional electrowinning methods [64] [71].

**Table VIII: Electrowinning system performance parameters**

<table>
<thead>
<tr>
<th>Electrowinning system performance parameters:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
</tr>
<tr>
<td>40-45 °C electrolyte</td>
</tr>
<tr>
<td>2.5V 11A</td>
</tr>
<tr>
<td>94% current efficiency</td>
</tr>
<tr>
<td>Zinc</td>
</tr>
<tr>
<td>30-50 °C electrolyte</td>
</tr>
<tr>
<td>5V 20A</td>
</tr>
<tr>
<td>95.5% current efficiency</td>
</tr>
</tbody>
</table>

4.9. Mixing

**Mixing of the metal bearing solution with the particle slurry**

The modular mixing components, described previously, functioned as designed. Qualitative observation of dyes in tracer studies showed complete mixing within the first section of four modular mixing components, and subsequent sections were assumed to aid in thorough mixing and contact. Sufficient mixing and contact were observed for the given experiments. The flexibility of the modular design would allow for more or less mixing for any given parameters and circumstance.

A computational method was also applied in order to ensure proper mixing. Godfrey proposed the following equations for modeling static mixers [72].

\[
\left( \frac{\sigma_B}{\sigma_u} \right)_{AR=L/D} = \left( \frac{\sigma_B}{\sigma_u} \right)_{AR=1} 
\]

(23)

\[
\sigma_u = \sqrt{x(1-x)}
\]

(24)
where \( \sigma \) is the standard deviation of concentration and the subscripts \( b \) and \( u \) are blended and unblended, respectively, \( AR \) is the aspect ratio, \( L \) is the length of the static mixer, \( D \) is the diameter, and \( COV \) is the coefficient of variation. For example, the calculations for experiment 37 are as follows:

The mass fraction of particles in solution, \( \bar{X} \), is given by:

\[
\bar{X} = \frac{C_{\text{dose}}}{C_A + C_{\text{dose}}}
\]  

where \( C \) is concentration in the dose and the solution. In experiment 37 \( C_{\text{dose}}=12 \text{g/L} \) and \( C_A=30 \text{g/L} \), and the desired coefficient of variation (COV) is <2%, therefore \( \sigma_b=0.0057 \) and \( \sigma_u=0.4517 \).

The modular mixing components most closely resemble a Kenics static mixer, and Godfrey gives the \( (\sigma_b/\sigma_u)_{AR=1} \) value for Kenics as 0.63. The diameter of the mixers is known, 0.0508 meters, therefore \( L \) can be solved for in the previous equations. In this example of Experiment 37, the required length is estimated to be 0.48 meters. The actual mixer length of 1.4 meters should be more than adequate, and was calculated as such for all experiments performed.
Mixing of loaded particles and solution with uncontaminated water within the column and collection module at the initiation of experiments

Mixing experiments carried out in order to establish a baseline were frustrated by variability of concentration data and failed to defined conditions with which to compare further experimentation. Seven baseline mixing experiment results are shown in Figure 66. The concentration is normalized as a ratio of the initial concentration, and measured as a function of the total cumulative flow. As the copper sulfate solution mixes with the water within the reactor, the copper concentration at the effluent initially increases consistently, however, after 10 liters have passed, the variability increases dramatically. No clear trend could be identified in order to differentiate dilution from adsorption phenomenon in temporal sampling and analysis.

4.10. Vertical Reactor

As discussed in section 4.6, modeling of the vertical reactor presented many challenges. This variability was not unexpected, as the scale of continuous flow reactors increases, the
departure from ideal behavior increases [73]. Even many of the established methods for modeling non-ideal flow, such as a dispersed flow model, fall short in this instance of non-constant cross-sectional area and multiple phases at varied velocities. Initial efforts to characterize the start-up of the process as a plug-flow reactor, and to relate that model to bench-scale data, were frustrated by non-conforming data. In lieu of a definitive model, a detailed mass balance was performed upon fifteen of the experiments investigating the start-up of the reactor and the data are summarized in Figure 67:

![Copper Mass Balance](image_url)

**Figure 67: Vertical reactor copper mass balance**
A near complete balance was achieved for each of the experiments, with an average of 97% closed balance. All the copper input was accounted for, either loaded on the particles, or in the effluent or concentrate feeds. Notice the diversion from some trends in Experiment 21, which was performed with a new batch of particles that evidently had different performance characteristics.

The initial concentration was a strong indicator for particle load (Figure 68). A clear trend of poor particle loading at low initial concentrations is evident. It should be noted these experiments were conducted over a range of flow, dose, and other parameters, which explains the scatter.

![Initial Concentration vs Loading](image.png)

**Figure 68: Initial concentration vs Particle loading**

Experiments designed to evaluate an extended residence time were conducted in order to assess the effect of extended residence time on loading at low concentrations. A pair of experiments with identical flow (1.9 LPM), dose (1.7g/L), and initial concentration (17.6 mg/L) were conducted with hydraulic residence times, to the sampling port, of 156 seconds and 314
seconds. Samples withdrawn at 210 seconds in the first and 330 seconds in the second, roughly the same state of completion, showed little difference in loading performance. In fact, the first experiment with twice the residence time had a slightly lower particle loading, at 0.089 mmole/g, as compared to 0.094 mmole/g for the shorter residence time.

Although a non-steady-state analysis of the start-up would be valuable, as a continuous flow process, a steady-state analysis would prove more relevant. Experiment 37 was the culmination of all previous work, and sought to establish steady state flow. A benchmark of low variability (<5% RPD) of effluent copper concentration over at least 5 minutes was established.

All previously defined optimal conditions were instituted for Experiment 37. Flow was set at 2.5 L/min, initial concentration was 127 mg/L and was adjusted to a pH of 3.5. The dose of particles was delivered at 2.8 g/L, with a total of 90 grams of particles, limiting the duration of the experiment. The electromagnetic coil was initially energized at 8 amps and 53 volts. Samples were collected at 2 to 3 minute intervals and analyzed by spectrophotometry. The findings are summarized in Figure 69:

![Steady State Operation](image)

**Figure 69: Vertical reactor copper concentration over time**
Steady state operation was achieved by around 450 seconds, which is consistent with the assumption that steady state will be achieved after 1 hydraulic residence time (463 seconds at 2.5 L/m). The magnetic collection module performed well, allowing 0.7 grams of rogue particles passed, or a collection efficiency of 99%. The magnetite particle reduced copper concentrations from 127 mg/L to around 85 mg/L, with a loading of around 0.23 mmole/g, which is close to the 0.3 mmole/g maximum loading previously documented.

A steady-state analysis of the continuous flow reactor can be performed from the Eulerian frame of reference via a simple mass balance. The concentration of the constituent of interest is dependent upon the independent variables of volume and time. The mass balance on a small element $\Delta V$ can be expressed as:

$$\Delta t \ Q \ C_{V,t} - \Delta t \ Q \ C_{V+\Delta V,t} + r \ \Delta V \ \Delta t = \nabla V \ [C_{t+\Delta t,V} - C_{t,V}]$$

(27)

where $\Delta t$ is the elapsed time interval, $Q$ is the flow rate, $C_{V,t}$ is the average concentration at $V$ over time interval $t \to t+\Delta t$, $C_{V+\Delta V,t}$ is the concentration evaluated at $V+\Delta V$ over $t+\Delta t$, $C_{t+\Delta t,V}$ is the average concentration in element $\Delta V$ at $t+\Delta t$, $C_{t,V}$ is the average concentration in $\Delta V$ at $t$, and $r$ is the average reaction rate. Dividing by $\Delta t$ and $\Delta V$, and taking the limit as $\Delta t$ and $\Delta V$ approach zero, the following equation is obtained:

$$-Q \frac{\partial C}{\partial V} + r = \frac{\partial C}{\partial t}$$

(28)

For a steady-state analysis, this equation will be equal to zero, as, by definition, the concentration at the effluent will not change with time. If integrated with respect to the concentration and multiplied by -1 the final form of the equation for the fate of the constituent of interest is obtained as:
\[ V = Q \int_{c_0}^{c} \frac{dC}{-r} \]  

(29)

Many assumptions must be satisfied in order to arrive at this equation, including no volume change, constant flow, and steady state operation. In addition to calculating the reactor volume, the steady-state reaction profile within the reactor can be determined from this equation. In order to assess the validity of this model, consider the parameters of Experiment 37:

- Flow was a constant 2.5 L/min
- Initial concentration was 127 mg/L, reduced to 105 mg/L by dilution of the slurry
- Steady-state concentration was 85 mg/L at the sample port
- The Langmuir reaction constant \( b \), for copper on magnetite, was reported to be 11.5647 [58]

When these parameters are entered into equation 29, the volume for Experiment 37 is calculated to be 4.3 liters. The actual volume of the reactor at the port is 4.9 liters, which is in close agreement.
5. Conclusions

5.1. Summary

Remediation of metal-containing industrial effluents presents both a technical challenge and an economic opportunity. Many industrial waste streams contain low level concentrations of metal ions requiring treatment prior to discharge. Existing treatment technologies are frustrated by disparate compositions and low metal concentrations. Although chemical precipitation is effective, it requires excessive reagents and discourages selective recovery. Conventional Ion-exchange requires a batch process with extensive operational and maintenance demands, and is rarely implemented in large-scale wastewater treatment. A continuous flow process capable of selective recovery would present many advantages over existing technologies.

This work examined and developed a continuous flow process for recovery of metal contaminants from industrial wastewaters with magnetic nanocomposites. The objective of this project was to not only prove the concept and elucidate the mechanisms, but to demonstrate potential for industrial application. All aspects of this process were investigated and optimized to the extent possible. Specific experimentation focused on magnetic nanocomposite ion exchange media development and synthesis, magnetic collection technology, metal recovery, and reactor and process development and modeling.

An effective ion exchange media was developed by Dr. Rosenberg’s lab with a magnetically susceptible magnetite core, durable silica shell, and polyallylamine functionalization. Metal ion loading behavior was demonstrated and modeled, with rapid kinetics and long-term regeneration potential. An in-line, water-cooled magnetic collection module was developed with collection efficiencies regularly exceeding 98%. A pilot-scale vertical reactor was developed and modeled, with demonstrated steady-state operation. Experiments showed
efficacy with surrogate solutions as well as actual mine affected waters. A viable metal recovery component of the process was demonstrated with an annular tangential-flow electrowinning technology.

The experimental results prove nanocomposite magnetic ion exchange media are a novel, effective, and reusable means of metal ion removal. Paired with the innovative electromagnetic collection module, a continuous flow process is made possible with low energy demand and pressure differential. This process is effective and predictable, and scalable to industrial applications. The system is amenable to automation, facilitating low maintenance requirements and allowing remote operation. The system is not confined by capacity or geometry. Scalability can be accomplished by multiple parallel columns. The configuration can be adapted to the application with options such as the compact helical configuration or the vertical configuration with its small footprint. In practice, multiple ions could be targeted with successive columns. Preconditioning and/or intermediate treatments such as chemical precipitation could aid in effective removal and recovery.

These collective findings substantiate the viability of a continuous flow process for recovery of metal contaminants from industrial wastewaters with magnetic nanocomposites. Several significant contributions were made to the fields of material science, wastewater treatment, process engineering, and hydrometallurgy. The magnetic collection system is state of the art and will allow industrial application of nano-scale adsorbents. Mechanisms elucidated in this work, such as the role of cooperative magnetophoresis, have bridged the gap between theory and application. Models developed in this work, such as the effects of magnetic agglomeration on adsorption, will facilitate accurate modeling and aid in adapting the system to a myriad of conditions.
The complete process, with all of the components is detailed in the process flow diagram in Figure 70. A simplified sequence of the overall process is given here:

- A slurry of magnetic nanocomposite ion exchange particles is introduced to the surrogate wastewater stream at the top of the platform.
- Functional groups impregnated on the surfaces of the ion exchange particles bond with metal ions as the particle-laden stream flows through the reactor.
- The electromagnet captures and retains the nanocomposite particles without impeding the wastewater flow.
- Valve positions are periodically changed to divert flow through a parallel magnetic module.
- The electromagnet is de-energized to release the particles, which are subsequently stripped, reconditioned, and returned to service.
Figure 70: Process flow diagram
5.2. Discussion of Conclusions

Within the limited scope of this research, metal recovery utilizing nano-scale magnetically susceptible particles in a continuous flow process has been shown to be a potentially viable wastewater treatment technology.

Nano-scale magnetite proved to be an ideal core material, as well as an effective standalone adsorption media. The 20-30 nm diameter particles responded well to the modifying chemistry, showed effective metal ion adsorption, and were sufficiently magnetically susceptible. The unique properties of nano-scale magnetite are paramount to the efficacy of this technology.

Agglomeration of the MNC particles was a persistent challenge to the research. However, the phenomenon was eventually understood and used as an advantage. Full dispersion and colloidal stability would offer greater flexibility in process design and increased adsorption performance. In the absence of sedimentation, a compact helical reactor design would present numerous advantages in industrial application. Modeling would be significantly simplified with a consistent, single phase velocity.

The poor performance observed at low concentrations, if not resolved, may be an impediment to industrial application. Many of the target metals, such as copper, require a near complete removal before discharge into natural waters. It is not entirely understood why particles are not reaching their potential loading capacities, even with extended residence times. Bench-scale experiments showed effective and fast loading in similar conditions and the cause of the disparity could not be identified.

The effects of competing ions were significant, but not unexpected. Without additional functionalization, such as the acetal modifications discussed previously, loading of non-target
ions was anticipated. In order to achieve effective metal recovery, selectivity will need to be addressed.

Modeling of a non-ideal reactor is challenging, however, the plug-flow reactor steady-state analysis proved suitable. A Eularian approach and mass balance led to a useful model that will allow process design for alternate conditions. Turbulent mixing and co-current multiphase flow resist definitive modeling; however, components of the system can be modeled individually to ensure performance, and the complete process can be evaluated separately in whole. Particle adsorption kinetics can be assessed to ensure proper residence time. Static mixers can be modeled to ensure proper contact. The magnetic collection module can be modeled to ensure proper collection efficiencies. Once these parameters have been satisfied, the complete reactor can be modeled, in a black-box fashion, in order to ensure overall performance.

Significant advancement was made with regard to magnetic separation of nanomaterials. The electromagnetic collection technology developed in this work is effective beyond laboratory scale and when paired with the appropriate particles performs at very high collection efficiencies. The use of the challenge solution for cooling of the electromagnet presents several advantages over other separation techniques. Direct water cooling allows for a significantly more powerful magnetic field, which in turn facilitates larger pipe diameters and higher fluid velocities. These are precisely the parameters required for a scale-up and industrial application of this process. In addition, the close contact afforded by placing the coil directly in the flow allows for greater collection efficiencies. Any heat transferred to the solution only serves to improve adsorption kinetics. Although high efficiencies have been achieved, further development of the technology will ensure negligible release of particles. In practice, additional electromagnet collection modules or permanent magnet scavengers will be required. As the concentration of particles in
the effluent decreases, the challenge of complete capture increases, as shown with the cooperative magnetophoretic model.

A physical model has been proposed for adsorption upon agglomerations about magnetic core wires. The model is based upon the geometry of particle buildup and the reduced surface area of a packed bed. This component is important to the overall process model, allowing an accurate representation of adsorption within the collection module to be integrated. This original work was not previously described in the literature.

Perhaps the most important findings in this work involve the compromises necessary for the exploitation of the properties of nano-scale adsorbents and the simultaneously inverse requirements for collection of these particles. The conflicting role of colloidal stability and magnetic separability provides only a narrow range of parameters for effective utilization. It was found that magnetite core in the 20-30 nm average diameter range prove sufficient specific surface area along with sufficient magnetic susceptibility. The domain grain size of magnetite superparamagnetism is approximately 30 nm, and maximization of this limit is advantageous. In this size regime, tremendous specific surface area is coupled with ample magnetic susceptibility. Detailed models of particle buildup within high gradient magnetic fields help with the understanding of efficient capture, and conversely, breakthrough. The role of cooperative magnetophoresis was demonstrated in this work, and represents an important finding. There is a “sweet spot” of particle dose, as a function of fluid velocity that optimizes capture.

The modular static mixing components performed well and represent another significant innovation. The ability to add static mixing to various pipeline configurations, including disparate sizes and radii, presents numerous opportunities previously unachievable. The
tunability of individual blade addition or subtraction allows for optimization not afforded with current technologies.

These collective findings substantiate the viability of a continuous flow process for recovery of metal contaminants from industrial wastewaters with magnetic nanocomposites. The advantages over conventional batch-process ion exchange are significant. Challenges associated with particle agglomeration, lack of selectivity, and poor performance at low concentration will need to be addressed before this technology will be adopted.

5.3. Limitations

A research project of this scale required a significant limiting of scope. The pilot scale studies included no less than 16 variables and only a cursory examination of the majority of these. A limited number of experiments were performed, by necessity, and a statistically significant analysis of the variables was not possible.

This research focused on a few target metal ions identified as plentiful in local mine affected waters. Numerous alternative metals and metalloids in a myriad of industrial waste streams present potential application within this technology. Most experimentation was conducted with surrogate solutions created with single metal, reagent grade chemicals. The effects of competing ions and/or actual waste water were not thoroughly studied. MNC particles were not synthesized for selectivity, and the results bore this out. Experiments with actual mine waters and mixed ions showed little to no selectivity.

Limited availability of the magnetic nanocomposite media led to abbreviated experiments. Three batches of less than 50 grams of MNC particles served as the basis of most
experimentation. The relatively large scale of experiments performed required sizable particle doses resulting in ephemeral experimentation.

No economic analysis was performed on this process, an important component of the evaluation of industrial applicability. The costs associated with the synthesis of the magnetic nanocomposites were unavailable, and likely irrelevant to the eventual costs associated with an industrial scaleup of the process. Specific scenarios and the potential for recovery of valuable commodities were too widely varied for accurate evaluation.

5.4. Recommendations for future work

Future experiments will assess the strip-regeneration process over many more cycles, and parameters will be optimized. Diminished loading will be quantified and modelled. Microscopy will be utilized to assess the durability of the shell.

Future experiments will further assess the magnetic collection system with attention to optimization. All experiments within this body of work utilized a single coil design operated at the maximum limit of the available power supply. Future work will examine coils of varying size and strength, over a range of operational parameters. It is anticipated experiments will show diminishing returns from more powerful magnets, based on the magnetic saturation of the magnetite cores, and these findings will define the upper limits of optimization. Magnetic core material characteristics will also be studied to provide the maximum collection efficiency.

Construction of a glass reactor was initiated and is ongoing. The design is nearly identical to the existing polymeric reactor, and the two reactors will function in tandem. The glass construction will allow for visual inspection of the process and will increase durability and cleanability.
Additional studies are required to quantify the mixing efficacy of the modular static mixing components. Experimental results will be compared with the proposed models. Typical mixing experiments will be performed and the performance of the components quantified and modeled.

Considerable work remains integrating the strip and regeneration cycle into the overall process. Optimization of the collection system will ensure minimum solution transport with loaded particles. Utilization of the strip and regeneration waste products will increase efficiencies.

Integration of the electrowinning circuit into the overall process requires additional experimentation. Possible intermediate steps to increase concentrations will be explored, such as membrane distillation [69]. Additional work remains in the electrowinning of other metals such as manganese [74] [75].

The potential for deleterious effects on the environment by rogue particle release will be studied. Ecological consequences of unavoidable minute releases, as well as potential accidental large-scale releases, will be evaluated. As an emerging technology, the ramifications of nano-scale particles in the environment have not been fully studied.

A detailed economic evaluation of the process will be applied to specific applications. The range of conditions and target metals will be evaluated to determine the parameters required for break-even operation. Costs associated with particle synthesis and reactor construction will be estimated.

Along with the metal recovery studied in this work, many alternative adsorption media and contaminant targets present opportunity for future study. Potential applications of the technology include:
• Laboratory and industrial separation of magnetically susceptible nano-particles. An efficient means of separating these materials has wide application.

• Removal and recovery of rare earth metals from dilute waste streams [31]. Mine-affected waters and other rare earth metal barring industrial effluents can be efficiently treated to levels safe for discharge.

• Removal and recovery of anions from dilute waste streams. Anionic contaminants, such as selenate in coal fired powerplant effluent, can be captured for disposal [76] [77] [78] [79] [80] [81] [82].

• Removal of oil droplets from produced water. Removal of colloidal oil droplets from produced water in the petro-chemical industry can be challenging and costly with current methods. Magnetically collected nano-composites could be an efficient alternative.

• Alternative coating on magnetic cores. Countless alternative coating materials are being explored for their unique properties. Natural and synthetic materials, such as chitosan, zeolite, ferrihydrite, and various polymers, are being investigated as potential adsorbents [83] [84] [85] [86] [87] [88] [89].
6. References/Bibliography


[79] W. Sun, W. Pan, F. Wang and N. Xu, "Removal of Se(IV) and Se(VI) by MFe2O4 nanoparticles from aqueous solution," *Chemical Engineering Journal*, vol. 273, pp. 353-362, 2015.


MTDEQ, "Priority Mine Sites," [Online]. Available:
7. Appendix A:

<table>
<thead>
<tr>
<th>Magnetic properties</th>
<th>The material is magnetic up to approximately 600°C (Curie point).</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emissivity - fully oxidized material</td>
<td>0.70</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CHEMICAL COMPOSITION</th>
</tr>
</thead>
<tbody>
<tr>
<td>C %</td>
</tr>
<tr>
<td>-----------------------</td>
</tr>
<tr>
<td>Nominal composition</td>
</tr>
<tr>
<td>Min</td>
</tr>
<tr>
<td>Max</td>
</tr>
</tbody>
</table>

Figure 71: Magnetic properties and composition of Kanthal A
<table>
<thead>
<tr>
<th></th>
<th>Inches</th>
<th>Meters</th>
<th>feet</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wire OD</td>
<td>0.05283</td>
<td>0.0013</td>
<td></td>
</tr>
<tr>
<td>Coil Width</td>
<td>4</td>
<td>0.1016</td>
<td></td>
</tr>
<tr>
<td>Coil OD</td>
<td>4.36902</td>
<td>0.111</td>
<td>Output</td>
</tr>
<tr>
<td>Coil ID</td>
<td>2.4</td>
<td>0.061</td>
<td>Constant</td>
</tr>
<tr>
<td>Wire length</td>
<td>15000</td>
<td>381</td>
<td>1250</td>
</tr>
<tr>
<td>windings (#)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Avg Circum.</td>
<td>10.6328</td>
<td>0.2701</td>
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</tr>
<tr>
<td>Avg Diameter</td>
<td>3.38451</td>
<td>0.086</td>
<td></td>
</tr>
<tr>
<td>Resistance R (Ω)</td>
<td>4.5791</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Current I (amp)</td>
<td>10</td>
<td>8.7353</td>
<td>8.7353 &lt;Select I for CC</td>
</tr>
<tr>
<td>Voltage (V)</td>
<td>45.791</td>
<td>40</td>
<td>&lt;Select V for CV</td>
</tr>
<tr>
<td>Mag Force B (T)</td>
<td>0.20622</td>
<td>0.1801</td>
<td></td>
</tr>
</tbody>
</table>

\[ V = I \times R \]

\[ B = \frac{\mu \times N \times I}{2 \times R} \]

\[ \text{1 meter} = 39.37 \text{ inches} \]
\[ \pi = 3.14159 \]
\[ \text{resistivity} (\rho) = 1.70E-08 \Omega m \quad \text{(for Cu)} \]
\[ \mu = 1.26E-06 \]

Figure 72: Electromagnetic coil modeling spreadsheet
Figure 73: Clamping mechanisms for magnetic collection module

Figure 74: Modular mixing component plans
Table IX: Composition of Fe₃O₄ nanoparticles

<table>
<thead>
<tr>
<th>Contents (Max %)</th>
<th>Fe₃O₄</th>
<th>&gt;98+</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>0.115</td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>0.005</td>
<td></td>
</tr>
<tr>
<td>SiO₂</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>SO₄</td>
<td>0.1</td>
<td></td>
</tr>
</tbody>
</table>
Figure 75: SDS for Fe₃O₄ Nanoparticles
8. Appendix B

Automation Code:

```
...
***
137 Module implementing MainWindow.
***

# from PySide.QtCore import Slot
140 from PySide.QtGui import QMainWindow
142 from PySide.QtGui import QApplication

# from .Ui_mainwindow_004 import Ui_MainWindow  # place to update GUI form
144 from .Ui_mainwindow_004 import Ui_MainWindow

### Required Imports ###
147 import Adafruit_ADS1x15  # for reading analog values
149 import csv              # for logfile creation
150 import logging         # for actual logging processes
151 import os              # for using paths
152 import random          # for creation of 'dummy' data
153 import serial          # for Serial object required in pH collection
154 import smbus           # for GPIO Expander Communication
156 import time            # for delays and system time in logs / on display
157 import threading       # for multithread processing
158 import queue           # for global access to boolean flags

### Global Variables ###

# Debug flags
161 ADC_DEBUG = False  # 1 for random temps, else 0 for ADC collection
162 pH_DEBUG = False   # 1 for random pH, else 0 for serial communication

# Log and Update Variables
164 log_interval = 1  # Time between log entries
165 log_append = "RPI_HMI_v1.0_LOG*"  # Name used to make logs more descriptive
166 update_GUI_interval = .05  # Time between GUI updates / run counts.

# Queues for multithread flag communication
169 log_q = queue.Queue(maxsize=1)  # used to stop thread
171 run_q = queue.Queue(maxsize=1)  # used to show if running or not
172 first_run = queue.Queue(maxsize=1)  # to denote first run or not
173 first_run.put(1)  # first run set as default

# Initialize log object Properties
175 logger = logging.getLogger(__name__)
177 logger.setLevel(logging.INFO)

# Creation of serial object that matches Orion star com specs
179 if not PH_DEBUG:  # will only create object if required
181 O8214 = serial.Serial(
182     port='/dev/ttyUSB0',  # may have to change...
183     baudrate = 9600,
184     parity=serial.PARITY_NONE,
185     stopbits=serial.STOPBITS_ONE,
186     bytesize=serial.EIGHTBITS,
187     timeout=1
188 )

### ADC Variables ###
190 # Setup of ADC
192 # Create an ADS1015 ADC (12-bit) instance on default channel 0x48
193 adc = Adafruit_ADS1x15.ADS1015()  # Used in get_V
194 Rs_1 = 9600
195 Rs_2 = 9900
196 num_to_avg = 10  # related to number of samples to take and average together
197 data_rate = 128  # actual sps of ADC
```
199  ''' Handling of Data Table Import '''
200  # Opening of file and reading
201  cwd = os.getcwd()
202  # use to have lookup table in separate directory
203  lookup_table = open(cwd+'/code/3950_NTC_loookuptable.csv', newline='')
204  table_data = csv.reader(lookup_table)
205  
206  # Creating blank lists for values
207  temperature_list = []
208  resistance_list = []
209  
210  # Populate lists with data
211  for row in table_data:
212      resistance_list.append(float( row[1] )*1000)  # convert to ohms
213      temperature_list.append( int( row[0] ) )
214  
215  ''' Associated Globals of KCF GPIO expanders and initial Configuration '''
216  # Physical device addresses
217  Valve_bus = 0x20  # Specific Device On IIC bus - mcp23008
218  Pump_Mag_bus = 0x21  # Specific Device On IIC bus - mcp23008
219  In_bus = 0x24  # Specific Device On IIC bus - mcp23017
220  
221  # Hex relating device to bit for easier coding
222  FP101 = 0x01
223  FP102 = 0x02
224  FP103 = 0x04
225  
226  EM201 = 0x10
227  EM202 = 0x20
228  
229  FV201 = 0x01
230  FV202 = 0x02
231  FV203 = 0x04
232  FV204 = 0x08
233  
234  # Pin registers on Out bus (O as in out)
235  pinDir_O = 0x00  # register for pin direction on 23008 (IOBXRX)
236  pinOut_O = 0x09  # register for pin outputs on 23008 (OLATX)
237  
238  # Pin registers on In Bus (A and B required for 16 channels)
239  pinDir_A = 0x00  # register for pin direction on A bus (IOBXRX)
240  pinDir_B = 0x01  # register for pin direction on B bus
241  
242  pinIn_A = 0x12  # register for pin inputs on A bus (GPIOX)
243  pinIn_B = 0x13  # register for pin inputs on B bus
244  
245  # creation of bus object - used to communicate over i2c bus
246  I2C = smbus.SMBus(1)
247  
248  # set all pins on output mcp as outputs and low - Forces Standby Initializing
249  I2C.write_byte_data(Valve_bus, pinDir_O, 0x00)
250  I2C.write_byte_data(Pump_Mag_bus, pinDir_O, 0x00)
251  
252  # set all pins on input mcp as inputs
253  I2C.write_byte_data(In_bus, pinDir_A, 0xFF)
254  I2C.write_byte_data(In_bus, pinDir_B, 0xFF)
255  
256  ''' Globals for GUI Update '''
257  var1 = var2 = var3 = 0  # Pump Status
258  var4 = var5 = var6 = var7 = 0  # Valve Status
259  var8 = var9 = 0  # EM status
260  var10 = var11 = var12 = 0  # data points
261  
262  ''' Thread Class Creations '''
263  class logThread (threading.Thread):
264      # Updated 11/19/16

Thread class that initializes log file, continuously gets current system
status, temperatures, and pH value, then populates log file, and
updates the GUI while global que

```
def __init__(self, parent, threadID, name):
    threading.Thread.__init__(self)
    self.threadID = threadID
    self.name = name
    self.parent = parent

    run(self):  # Action taken by thread upon start
        print("*Running %s" % self.name)
        initializeLog()
        print("FILE initialization, Headers created, Logging Started")
        self.parent.Log_Status.setText("Log Running")
        printLog(self.parent, self.name, i)  # 'Endless' Loop - exits via flag
        print("*Stopping" + self.name)
        self.parent.Log_Status.setText("Log Standby")
        QApplication.processEvents()  # forces update of GUI
```

```
class cycleThread(threading.Thread):
    # init updated 12/28/16
    ""
    Thread class forces mode logic to output bus via runmode function and
    'counts' time spent in each mode in order to updates gui.
    ""
    __init__(self, parent, threadID, name):
        threading.Thread.__init__(self)
        self.threadID = threadID
        self.name = name

        # Gets total Cycle time from GUI
        # clever conversion of str -> float -> int
        self.Init_Time = int(float(parent.Init_tot.text()))
        self.Side1_Time = int(float(parent.Side1_tot.text()))
        self.Side2_Time = int(float(parent.Side2_tot.text()))
        
        # +1 at the end due to combo box behavior, index starts at 0
        # but display values start at 1.
        self.Cycles = int(parent.cb_repeat_cycle.currentIndex()+1)
        self.parent = parent

        def run(self):
            # Runs desired modes in order while checking queus.
            print("*Running %s" % self.name)

            # runMode Arguments: Valve_bus, PM_bus, mode_time, CT display, parent
            # Initialize Mode
            if self.Init_Time:
            runMode(0x05, 0x01, self.Init_Time, self.parent.current_Init_Time,
                self.parent)

            cycle_counter = 0
            while cycle_counter < self.Cycles:  # Start of Cycle
                # Side 1 Run
                if self.Side1_Time:
                    runMode(0x05, 0x17, self.Side1_Time, self.parent.current_Side1_Time,
                        self.parent)
                # Side 2 Run
                if self.Side2_Time:
                    runMode(0x08, 0x27, self.Side2_Time, self.parent.current_Side2_Time,
                        self.parent)
```

cycle_counter += 1

systemOff()

print("**Stopping " + self.name + ". Entering update only mode...")

while not run_q.empty(): ## run_q == 1
    #NOTE: Change of system_time signal related to Progress bar / GUI update
    self.parent.system_time.setText("Update GUI!")
    self.parent.system_time.setText(" ")
    time.sleep(update_GUI_interval)

    *** CTRL functions ***

    def runMode(V_busout, FM_busout, mode_Time, CT_display, parent):
        # Updated 12/18/16
    ***

    if not run_q.empty(): ## run_q == 1
        # Pacing state to output busses
        I2C.write_byte_data(Valve_bus, pinOut_0, V_busout)
        I2C.write_byte_data(Pump_Mag_bus, pinOut_0, FM_busout)

        time_start = time.time() # for start time
        waited = 0

        # Entering wait loop
        while waited < (mode_Time* update_GUI_interval* .5):
            if run_q.empty(): ## run_q == 0
                break
            else:
                tot_time = time.time() - time_start
                #print('update time: ', tot_time) # for debug
                if tot_time < update_GUI_interval:
                    time.sleep(update_GUI_interval - tot_time)
                    waited += update_GUI_interval
                else:
                    print('GUI update taking longer than update interval')
                    waited += tot_time

                time_start = time.time() # for subsequent repeats
                wait_String = '{:.2f}'.format(waited)

                CT_display.setText(wait_String)

        # update of total progress counter
        try:
            current_tot = float(parent.current_Rep_Cycle.text())
            current_tot += update_GUI_interval
        except ValueError:
            current_tot = update_GUI_interval;

        parent.current_Rep_Cycle.setText('{:.2f}'.format(current_tot))

        #NOTE: Change of system_time signal related to Progress bar & GUI update
    #parent.system_time.setText("Update Progress Bars & GUI!")
    #parent.system_time.setText(" ")

    else: #if run_q empty, system goes to standby mode - all off
        systemOff()}
def systemOff():
    # Updated 11/19/16
    """ Sets system to safe off/standby mode. """
    I2C.write_byte_data(Valve_bus, pinOut_0, 0x00)
    I2C.write_byte_data(Pump_Mag_bus, pinOut_0, 0x80)

    """ DATA functions """
    # As of 12/18/16 : debug flags added. needs real pH functions
    def calc_temp(Vcc, Vadc, Rs):
        """
        Calculates temperature of thermistor based off the VCC and Vadc given known
        Shunt Value. Physically built as:
        VCC----Rs---/---Thermistor----GND
        Uses global temperature and resistance lists in order to
        perform linear approximation.
        """
        R_t = (Vadc*Rs) / (Vcc-Vadc)
        upper_ndx =[ ]
        while R_t < resistance_list[upper_ndx]:
            upper_ndx += 1
        lower_ndx = upper_ndx-1
        """ linear approximation variables for cleaner equation
        CH = temperature_list[upper_ndx]
        CL = temperature_list[lower_ndx]
        RH = resistance_list[upper_ndx]
        RL = resistance_list[lower_ndx]
        RM = R_t
        """ linear approximation calculation
        CH = ( (CH-CL) * (RH-RL) ) / (RH-RL) + CH
        return CM

    def get_V(A_IN, GAIN, RATE, FS_V, num_to_avg):
        """
        Function to get a voltage average from the ADS1015, uses global
        ADC variables.
        """
        Vadc = [ ]; V_DN = [ ]; ndx=3
        while ndx < num_to_avg:
            V_DN = adc.read_adc(A_IN, gain=GAIN, data_rate=RATE)
            Vadc = Vadc + (V_DN/2047) * FS_V
            ndx += 1
        return Vadc/ndx

def getpH():
    # Used to generate random pH for logging purpose
    pH = random.random()*2+7
    return pH

def getTemp():
    # Used to generate random temps for logging purpose
    temp = random.random()*5+65
    return temp

    """ GUI functions """
    # Updated 11/19/16
    def convert_time(min, sec):
        return min, sec
156

```python
# Updated 11/19/16
*** Takes int values min/sec and returns string of total time ***
total_time = min*60
total_time = total_time + sec
return str(total_time)+':00'  # string because being passed to GUI

def discoverMode(system_sum):
    # Updated as of 11/19/16
    *** Returns mode string based on sum of system input buses. ***
    ## NO FIGHTING INPUTS ALLOWED ##
    if system_sum == 0x00:
        status = "System in Standby"
    elif system_sum == 0x06:
        status = "System Initializing"
    elif system_sum == 0x1C:
        status = "Side 1 Running"
    elif system_sum == 0x31:
        status = "Side 2 Running"
    else:
        status = "NOTICE: Unknown Mode"
    return status

def percentCheck(currentTimeLabel, totalTimeLabel):
    # Updated 11/19/16
    *** Used to update progress bar percents and accounts for spacer dashes "-", and occasional divide by 0 via try except.***
    try:
        progPercent = float(currentTimeLabel) / float(totalTimeLabel) * 100
        progPercent = int(progPercent)
    except (ValueError, ZeroDivisionError):
        progPercent = 0
    return progPercent

def resetGUI(self):
    # Updated 11/19/16
    *** Function to reset GUI for non-running interaction and display ***
    # enable alteration of times
    self.cb_Init_time_min.setEnabled(True)
    self.cb_Init_time_sec.setEnabled(True)
    self.cb_side1_time_min.setEnabled(True)
    self.cb_side1_time_sec.setEnabled(True)
    self.cb_side2_time_min.setEnabled(True)
    self.cb_side2_time_sec.setEnabled(True)
    self.cb_repeate_cycle.setEnabled(True)
    # set current times and Cycle to "-"
    self.current_Init_Time.setStrText("-")
    self.current_Side_1_Time.setStrText("-")
    self.current_Side_2_Time.setStrText("-")
    self.current_Rep_Cycle.setStrText("-")
    # set total times to "-"
    self.Init_tot.setText("-")
    self.Side_1_tot.setText("-")
    self.Side_2_tot.setText("-")
    self.Rep_Cycle_tot.setText("-")
def returnStatus(value, option):
    # Updated 03/19/17
```
def setGUI(self):
    # Updated 11/19/16
    ***
    Function to set GUI for run time interaction (i.e. changes disabled)
    and compute/display total mode and cycle times
    ***
    # disable alteration of times
    self.cb_init_time_min.setEnable(False)
    self.cb_init_time_sec.setEnable(False)
    self.cb_side1_time_min.setEnable(False)
    self.cb_side1_time_sec.setEnable(False)
    self.cb_side2_time_min.setEnable(False)
    self.cb_side2_time_sec.setEnable(False)
    self.cb_repeat_cycle.setEnable(False)

    # Set total times to correct number from combo box for use in cycle thread
    cumulative_time = 0  # place holder for cumulative progress bar time
    cycles_tot = self.cb_repeat_cycle.currentIndex() + 1  # for multiplication

    # Get time from GUI combobox inputs as total seconds - initialize time
    init_time_str = convert_time(int(self.cb_init_time_min.currentText()),
        int(self.cb_init_time_sec.currentText()))
    # echo to GUI
    self.Init_tot.setText(init_time_str)
    # add to cumulative time
    cumulative_time += float(init_time_str)

    # Get time from GUI combobox inputs as total seconds - side 1 time
    side1_time_str = convert_time(int(self.cb_side1_time_min.currentText()),
        int(self.cb_side1_time_sec.currentText()))
    # echo to GUI
    self.Side_1_tot.setText(side1_time_str)
    # add to cumulative time
    cumulative_time += float(side1_time_str)*cycles_tot

    # Get time from GUI combobox inputs as total seconds - side 2 time
    side2_time_str = convert_time(int(self.cb_side2_time_min.currentText()),
        int(self.cb_side2_time_sec.currentText()))
    # echo to GUI
    self.Side_2_tot.setText(side2_time_str)
    # add to cumulative time
    cumulative_time += float(side2_time_str)*cycles_tot

    # Set cumulative time to total time on GUI
    self.Rep_Cycle_tot.setText(str(cumulative_time))

    *** LOG functions ***
def initializeLog():
    # Updated as of 12/17/16

    logName = time.strftime('%Y.%m.%d_%H.%M.%S_') + log_append + '.csv'

    # Generate Log name based on current time and date + log_append ''

    # Custom Header Creation ''

    colNames = ('Date[YYYY.MM.DD],Time[HH:MM:SS.ms],Log Number, 'FP101,FP102,FP103,' # var 1-3
                'FPV01,FPV02,FPV03,FPV04,' # var 4-7
                'EM201,EM202,' # var 8-9
                'Temp1,Temp2,pH') # var 10-12

    # Specify Column Log names - Notice no spaces between commas on purpose for format

    customHeader = csv.writer(csvfile, delimiter=' ',
                               quoting=csv.QUOTE_MINIMAL)

    # Create Csv file with custom header

    colNames = [colNames]
    customHeader.writerow(colNames)

    # '' Configure Logging ''

    # Create Handler

    handler = logging.FileHandler(cwd + '/' + logName) # sets where log is to be written

    handler.setLevel(logging.INFO) # sets level of logs to collect

    def configureLogging():
        # Create a logging format
        # Notice the removed space before %H to prevent auto format of csv
        # This causes hours to display wrong in excel however, logged data is correct
        formatter = logging.Formatter('%(asctime)s,%(message)s',
                                      datefmt='%Y.%m.%d,%H:%M:%S')

        # Set format to handler

        handler.setFormatter(formatter)

        # In order to account for multiple logging runs per session:
        # add handler to logger, remove old handler if not first_run

        if first_run.empty(): # first_run --
            logger.removeHandler(logger.handlers[0]) # clear previous handler
            logger.addHandler(handler) # add new handler

        else: # first_run --
            logger.addHandler(handler)

        first_run.get() # Remove first_run Flag

    def printLog(parent, threadName, logRun): #modified from multithread_02
        # Updated as of 12/28/16

        # To use global variables instead of locals
        global var1, var2, var3, var4, var5, var6, var7, var8, var9, var10
        global var11, var12

        ndx = 1 # Used as a counter
time_start = time.time() # for initial cycle time

        # logRun passed in as 1
        while logRun:
            # will exit on #

            if not log_q.empty():
                # log_q --

                if log_q.get(): # if number is not #, clear queue and stop log
                    logRun = # # breaks out of outer while loop

                print("(exitFlag True, logRun == ")

            continue
...  

This is where values to be logged are gathered.  
Place holder function calls for getTemp and getPH are here.  
Also creates log string written to csv log.  

# Get Current Bus Values  
current_bus_A = I2C.read_byte_data(In_bus, pinIn_A)  
current_bus_B = I2C.read_byte_data(In_bus, pinIn_B)  

# Extract individual device status 'and True' required for 1 or 2  
var1 = int( (current_bus_B & FP101) and True )  
var2 = int( (current_bus_B & FP102) and True )  
var3 = int( (current_bus_B & FP103) and True )  

var4 = int( (current_bus_A & FP201) and True )  
var5 = int( (current_bus_A & FP202) and True )  
var6 = int( (current_bus_A & FP203) and True )  

var7 = int( (current_bus_A & FP204) and True )  
var8 = int( (current_bus_B & EM201) and True )  
var9 = int( (current_bus_B & EM202) and True )  

if ADC_DEBUG:  
    var10 = getTemp()  
    var11 = getTemp()  
else:  
    # place for temperature calls  
    Vcc = round( get_V(, 2/3, data_rate, 6.144, num_to_avg), 4)  
    # Settings  
    to read Vcc A_in_0  
    Vadc_1 = round( get_V(1, 1, data_rate, 4.096, num_to_avg), 4)  
    # Settings  
    to read A_in_1  
    var10 = round( calc_temp(Vcc, Vadc_1, Rs_1), 3)  
    # Settings  
    to read Vcc A_in_0  
    Vadc_2 = round( get_V(2, 1, data_rate, 4.096, num_to_avg), 4)  
    # Settings  
    to read A_in_2  
    var11 = round( calc_temp(Vcc, Vadc_2, Rs_2), 3)  

if PH_DEBUG:  
    var12 = getPH()  
else:  
    OS214.write(b'GETMEAS\r\n')  
    # Sending command to have device send current measurement  
    x=OS214.readline()  
    while (sys.getsizeof(x) < 80):  
        x = OS214.readline()  
    data = x  
    # required type casting for split command  
    parsed = x.str.split("\"\")  
    # parse data  
    #print(x)  
    # NOTE: Debug # raw data print  
    print(""Parsed pH: ", parsed[8])  
    var12 = float(parsed[8])  

# Create String To Log consisting of ndx plus 12 vars.  
logger.info("%d,%d,%d,%d,%d,%d,  
    'd,%d,%d,%d,%d,%d,  
    ndx, var1, var2, var3, var4, var5,  
    var6, var7, var8, var9, var10, var11, var12)  

print(""log \d logged" & ndx)  
    # status print for debug
# wait for an exact time so log had reduced jitter
tot_time = time.time() - time_start

# More accurate sleep time and check if log taking too long.
if tot_time > log_interval :
    print('Log taking longer than log interval to make...')
    print('total time: %f' % tot_time)
else:
    time.sleep(log_interval-tot_time)

ndx += 1
time_start = time.time() # for complete loop process timing

'""" GUI MainWindow class """
# Updated 11/19/16
class MainWindow(QMainWindow, Ui_MainWindow):
    # Updated 11/19/16
    ***
    Main GUI that will take user input for cycle times, display current system
    status and most recently logged temperature and pH
    ***
    def __init__(self, parent=None):
        """ Automatically generated Constructor """
        @param parent reference to the parent widget
        @type QWidget
        """
        super(MainWindow, self).__init__(parent)
        self.setupUI(self)

        self.setWindowTitle("RPI RMI v1.0") # Title creation

def closeEvent(self, event):
    # Updated 12/26/16
    """ Tasks to carry out if 'X' clicked """
    systemOff() # puts system into standby mode
    if not run_q.empty():
        run_q.get() # remove item from run_q
    if log_q.empty():
        log_q.put(1) # putting something in log_q stops loggings
    time_now = time.time() - time_start
    while time_now < log_interval*2:
        self.System_Mode.setText("Shutting Down...")
        time_now = time.time() - time_start
        QApplication.processEvents() # forces update of GUI?

    event.accept()

# Slot ()
def on_start_bta_released(self):
    # Updated 11/19/16
    """
    On Start btn press :
    if run_q is empty
        disable alteration of cycle times via setGUI
    put 1 in run_q to signify running
    display system status as started
    create and start the logging thread
    create and start the mode thread that will take the times entered
    in on GUI as parameters.
else: run_q has something in it -> already running

if run_q.empty():
    setGUI(self)
    run_q.put(1)
    self.System_Mode.setText("Started")
    log_thread = logThread(self, 1, "Logging Thread")
    log_thread.setDaemon(True) # Stops thread if main thread stopped
    log_thread.start()

    cycle_thread = cycleThread(self, 2, "Mode Cycle Thread")
    cycle_thread.setDaemon(True)
    cycle_thread.start()

else: # run_q has something in it ->
    self.System_Mode.setText("Already Running")

@Slot()
def on_stop_btn_released(self):
    # Updated 11/19/16
    ***
    on stop btn press:
    if running:
        removed running flag from run_q
        turn system to off/standby state
        sleep so log can reflect off state
        stop log by putting 1 in log_q
        reset GPIO pins to default status
        change systems status on GUI to standby
        reset GUI

    else: (already stopped)
    change system status to reflect already stopped

    ***
    if not run_q.empty(): # if run_q has something in it
        run_q.get() # remove item from run_q
        systemOff()
        time.sleep(log_interval) # wait for system to be shown in off state for 1 sec
        log_q.put(1) # putting something in log_q stops loggings
        self.System_Mode.setText("System Stopped")
        resetGUI(self)

    else: # run_q already empty ->system stopped
        self.System_Mode.setText("System Already Stopped")
        systemOff() # for double stop...

@Slot(str)
def on_system_time_textChanged(self, p0):
    # Updated 12/28/16
    ***
    Slot designed to update progress bars from main GUI thread -for safety.
    Will update every wait update interval as slot signaled in runMode function.
    ***
    time_start = time.time()
    self.Init_prog.setValue( percentCheck(self.current_Init_Time.text()),
                              self.Init_tot.text())
    self.Side_1_prog.setValue( percentCheck(self.current_Side_1_Time.text()),
                              self.Side_1_tot.text())
self.Side_2_prog.setValue( percentCheck(self.current_Side_2_Time.text()),
self.Side_2_time.text())
self.Total_prog.setValue( percentCheck(self.current_Rep_Cycle.text()),
self.Rep_Cycle_time.text())

# Get Current Bus Values For Mode Discovery
current_bus_A = I2C.read_byte_data(In_bus, pinIn_A) # bus with valves
current_bus_B = I2C.read_byte_data(In_bus, pinIn_B) # bus with pumps + magnets
self.System_Mode.settext( discoverMode( current_bus_A + current_bus_B ) )

# update top GUI info field
self.as_of_time.setText("System Status as of \* time.strftime("%B %d, %Y at \\
hh:mm:ss")")

# update individual device status on GUI
self.FP101_val.setText( returnStatus(var1, [ ] )
self.FP102_val.setText( returnStatus(var2, [ ] )
self.FP103_val.setText( returnStatus(var3, [ ] )

self.FV201_val.setText( returnStatus(var4, 'open')
self.FV202_val.setText( returnStatus(var5, 'open')
self.FV203_val.setText( returnStatus(var6, 'open')
self.FV204_val.setText( returnStatus(var7, 'open')

self.EN201_val.setText( returnStatus(var8, [ ]
self.EN202_val.setText( returnStatus(var9, [ ]

# update Temperatures
tempString = str(var10)
self.temp_val_1.setText(tempString[4]))

tempString = str(var11)
self.temp_val_2.setText(tempString[4])

# update pH
pHString = str(var12)
self.pH_val.setText(pHString[6])

if (time.time()-time_start > update_GUI_interval):
    print("GUI update longer than update interval...")

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