MONTANA RESEARCH AND ECONOMIC DEVELOPMENT INITIATIVE (MREDI)

Recovery of Metal Contaminants from Industrial Wastewaters with Magnetic Nanocomposites in a Novel Continuous Flow Process System

Quarterly Progress Report

January 1 to March 31, 2017

Submitted to:

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RECOVERY OF METAL CONTAMINANTS FROM INDUSTRIAL WASTEWATERS WITH MAGNETIC NANOCOMPOSITES IN A NOVEL CONTINUOUS FLOW PROCESS SYSTEM

SUMMARY

This quarterly progress report covers the project period from January 1, 2017 to March 31, 2017. Further progress has been made toward completion of the five project objectives. The progress made toward achieving each objective is described in this report. More detailed data related to the results described in this report are available on request.

PERSONNEL/HIRES

Montana Tech (MTech) added a graduate student and an undergraduate student to their project team effective January 2017. Dr. Katherine Zodrow and post-bac research assistant Christina Eggensperger joined the Montana Tech project team; their responsibilities are to 1) investigate the nanoparticle agglomeration issue and 2) investigate potential methods for further concentrating the metal tenor in the continuous flow reactor strip solutions in preparation for metal recovery via electrowinning. The current team rosters are listed below.

MTECH TEAM; Jerry Downey, PI

- Hsin Huang, Co-PI, Professor, Metallurgical and Materials Engineering (M&ME)
- Alysia Cox, Co-PI, Assistant Professor, Chemistry and Geochemistry
- Katherine Zodrow, Assistant Professor, Environmental Engineering
- David Hutchins, Materials Science Ph.D. student
- Renee Schmidt, Geochemistry M.S. student
- Maureen Chorney, M&ME M.S. student
- Christina Eggensperger, Environmental Engineering post-bac student
- Jared Geer, M&ME undergraduate student
- Elizabeth Raiha, M&ME undergraduate student
- Auva Speiser, M&ME undergraduate student

UM TEAM; Ed Rosenberg, PI

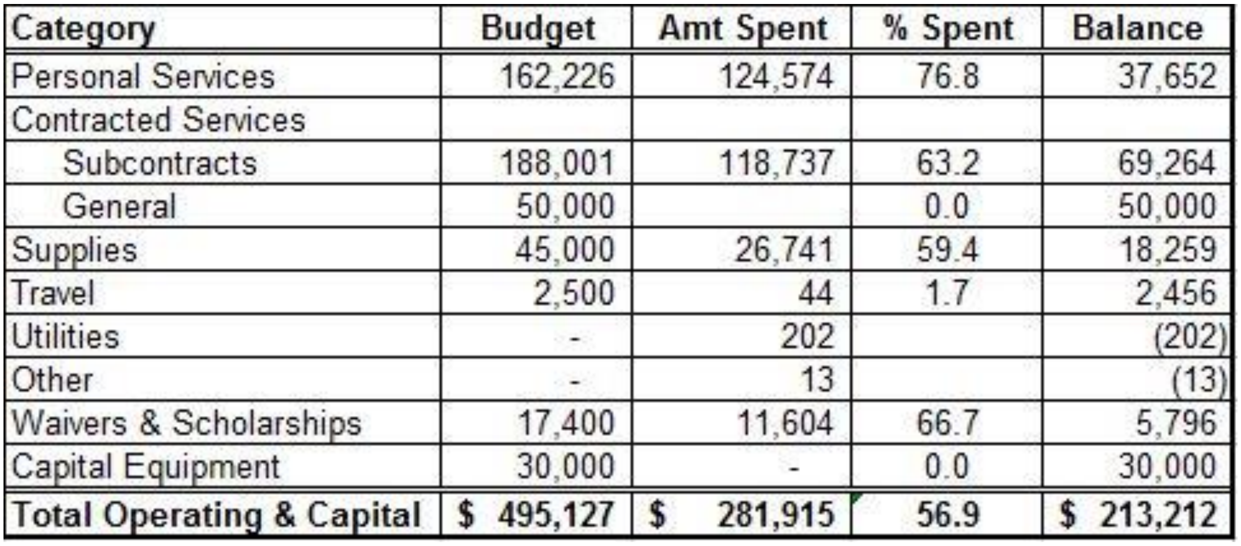
- Ryan Latterman, Post-Doctoral Research Associate
- Two undergraduate students

EXPENDITURES

Total project expenditures of $281,915 have been recorded through March 31, 2017, representing approximately 57% of the overall project budget of $495,127. The spending increased during the past quarter due to the construction and implementation of the 4th generation reactor and the advanced spending rate is expected to again accelerate during the next (final) quarter of the project. The entire capital equipment budget ($30,000) was expected to be consumed during the past quarter. Equipment procurement had been deferred because the MTech team wanted to confirm the modified (4th generation) reactor design before committing funds to the acquisition of the new equipment. The design has been finalized and the team is waiting the vendor bid.

The project budget and expenditures are summarized in Table 1. All phases of the project remain within budget.

Table 1 – Summary of Project Expenditures through March 31, 2017*



Category	Budget	Amt Spent	% Spent	Balance
Personal Services	162,226	124,574	76.8	37,652
Contracted Services				
Subcontracts	188,001	118,737	63.2	69,264
General	50,000		0.0	50,000
Supplies	45,000	26,741	59.4	18,259
Travel	2,500	44	1.7	2,456
Utilities	-	202		(202)
Other	-	13		(13)
Waivers & Scholarships	17,400	11,604	66.7	5,796
Capital Equipment	30,000	-	0.0	30,000
Total Operating & Capital	**$ 495,127**	**$ 281,915**	**56.9**	**$ 213,212**

***totals do not include expenditures that did not enter the accounting system prior to March 31.**

MTECH TEAM

- Total Budget: $307,126; total expenditures of $163,484.74 (53.2%) through March 31, 2017.
- Personnel Services will spike in the final quarter because of summer salaries for participating faculty and available work hours for student employees double (from 20 to 40 hours/week).
- Expenditures for Supplies and General Contracted Services surged in the past quarter as the focus of the research transitioned from reactor design and development to experimental determination of metal removal efficiencies. The spending rate in this category is expected to increase again in the final quarter.
- The team is awaiting bids for the 4th generation flow reactor; the reactor cost will consume the $30,000 capital equipment budget.

UM TEAM

- Total Budget: $188,001; total expenditures of $118,432 (63.0%) through February 28, 2017.

- All UM invoices forwarded to MTech have been approved for payment.

PROGRESS TOWARD MILESTONES

The following sections describe progress according to the specific project Objectives 1 through 5.

OBJECTIVE 1: WASTEWATER CHARACTERIZATION

MTECH TEAM; Alysia Cox (Co-PI)

- Since the beginning of the project, the Laboratory Exploring Geobiochemical Engineering and Natural Dynamics (LEGEND) sampled local surface waters on six different days (once every ~3 months, 6 sites per day) for a total of 30 samples. Nine flooded underground mine complexes have been sampled for water quality to date (Anselmo, Kelley, Steward, Ophir, Travona, Emma, Pilot Butte, Orphan Boy, and Orphan Girl). The Horseshoe Bend water treatment plant has also been sampled. The mines can be classified into three geochemical zones, ranging from low pH, high metals, low sulfide in the East Camp mines to high pH, lower metals, and high sulfide in the Outer Camp mines (Figures 1 and 2). Copper concentrations range from tens of nanomolal to micromolal (from less than 1 – 49 ppb) in various Montana waters sampled (Figure 3).
- Renee Schmidt is writing her MS in Geochemistry thesis and is expected to defend on May 22nd or 23rd.

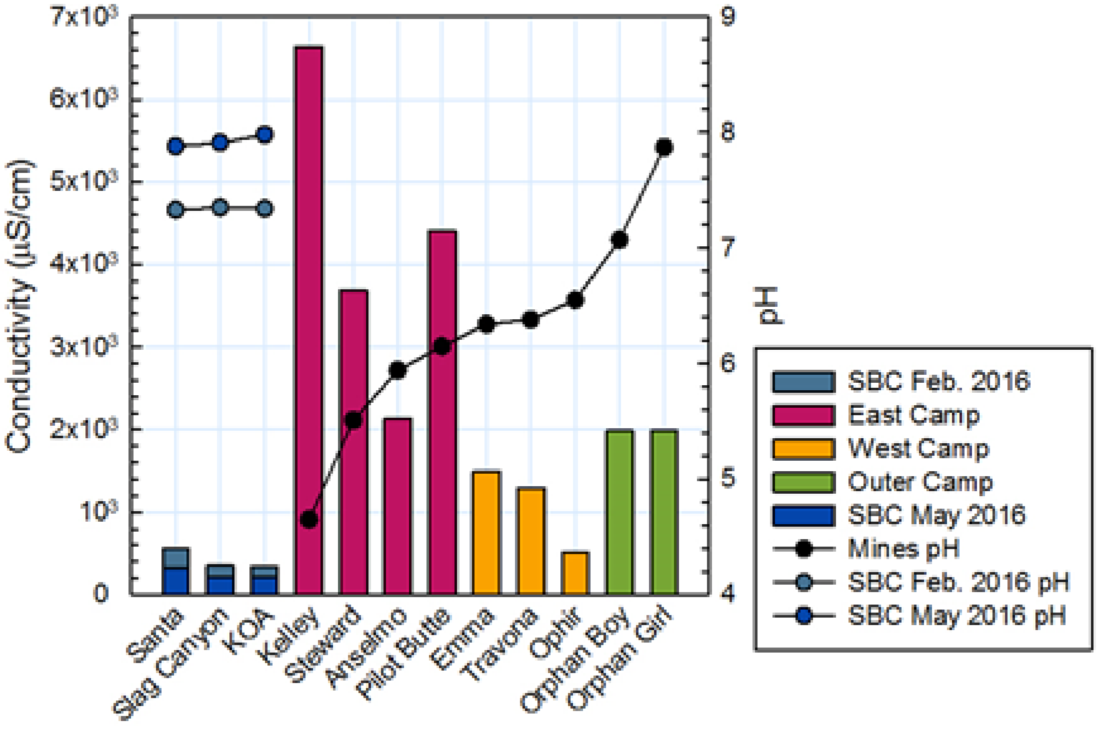


Figure 1: Conductivity and pH trends in the mines and Silver Bow Creek (SBC) (Schmidt, in prep).

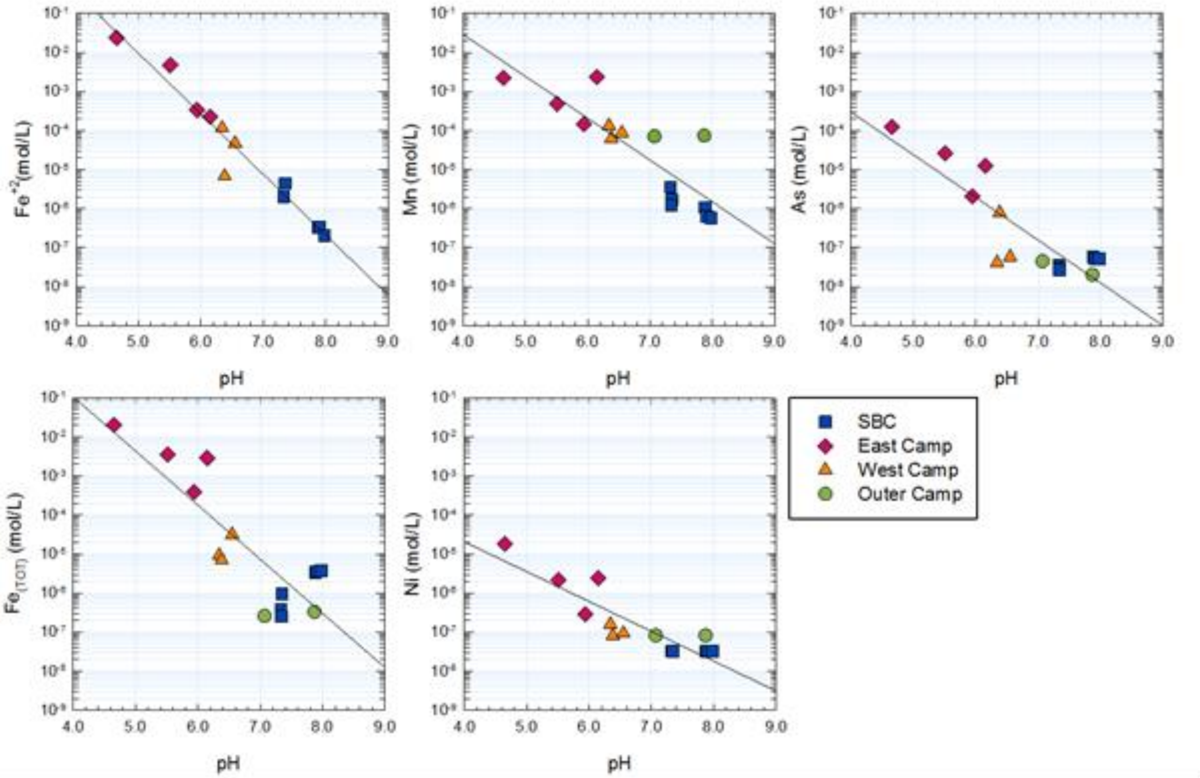


Figure 2: pH trends of selected dissolved metals (Schmidt, in prep).

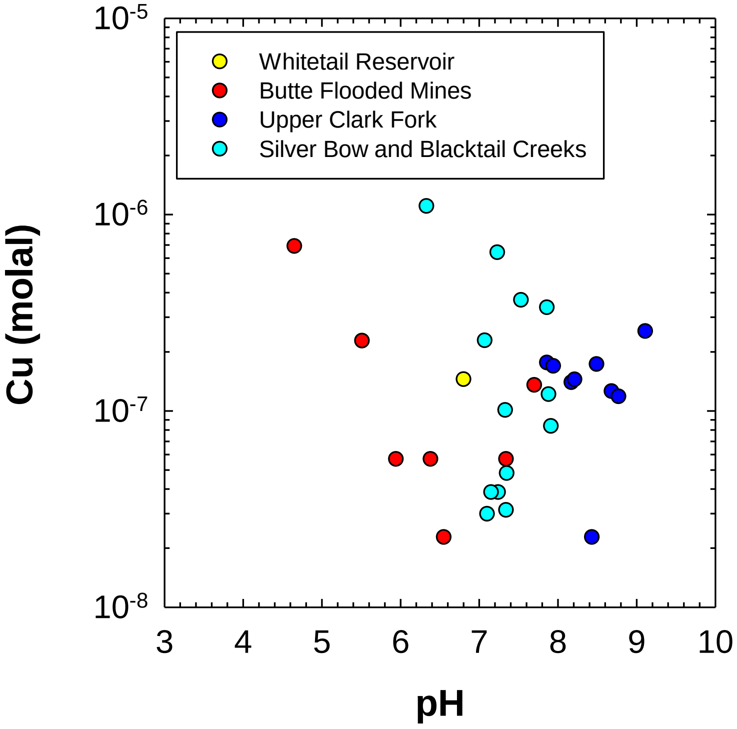


Figure 3: Total dissolved copper vs. pH for various Montana waters

OBJECTIVE 2: MAGNETIC NANOCOMPOSITE SYNTHESIS

UM TEAM; Ed Rosenberg (PI) and Ryan Latterman

1. 40g scale up of polyethylenimine functionalized magnetic nanoparticles

Previously, our synthetic work focused on scaling up the production of core shell magnetic nanoparticles (CSMNs) functionalized with poly(allylamine) (PAA). PAA is a polymer that contains only primary amines while polyethylenimine (PEI) contains primary, secondary and tertiary amines. In past research that utilized silica polyamine composites (SPCs), the Rosenberg lab used both PEI and PAA when developing strategies for further functionalization with metal specific ligands. This quarter we successfully scaled up the synthesis of CSMNs functionalized with PEI and provided our collaborators at Montana Tech with a 40g sample. The copper batch capacities of PEI-CSMNs were lower than PAA-CSMNs, which mirrors what was found for SPCs. Using a 60,000 MW PEI polymer, batch capacities of 0.200 mmol/g were achieved (batch conditions: 1500 ppm Cu^{2+} at pH 4.5). Because of the presence of secondary and tertiary amines on the surface of PEI-CSMNs, a small but still potentially useful copper batch capacity at pH 2 was also achieved (0.050-0.100 mmol/g). Another potentially useful characteristic of PEI-CSMNs is their tendency to stay suspended in aqueous solutions more effectively than PAA-CSMNs. Depending on the final design of the flow reactor, better suspension in solution may prove useful.

2. Copper capacity and cost comparison of aqueous commercial nanoparticles vs dry powder

Our current strategy for large-scale production involves utilizing a commercial source (Sky Spring Nanomaterials) of magnetic nanoparticles that we receive in dry powder form. We have scaled up our reaction conditions to 40g at a time and have produced CSMNs that have useful copper capacities and are able to be captured in the flow reactor system. However, because the particles start as a dry powder, they are quite difficult to suspend thoroughly in a solution before functionalization procedures. Therefore, we suspect that we are not utilizing the full surface area to volume ratio potential of the nanoparticles. A commercial source of aqueous nanoparticles was identified and a small sample of these particles were purchased in order to compare particle size and copper batch capacities to our current method of starting from dry particles. A copper capacity of 0.658 mmol/g was achieved (5g scale reaction) using the new source of aqueous nanoparticles compared to our previous result of 0.500 mmol/g. Although a larger capacity was achieved, the cost difference between dry and aqueous nanoparticles seems cost-prohibitive (dry powder: $0.34/g, aqueous: $7.00/g). However, in the future, if the larger copper capacities outweigh the costs of purchasing aqueous nanoparticles, it may be beneficial to start with aqueous nanoparticles.

3. Small-scale modification of polyamine surface with bromoacetic acid

In order to capture metals at a pH lower than 4, one strategy involves modifying the polyamine surface with carboxcylic acid groups. A primary focus of this past quarter was to investigate the optimal reaction conditions for the coupling of amine groups with bromoacetic acid (1-2 g). Figure 4 shows the general reaction scheme for the functionalization of amine groups starting with both PAA and PEI-CSMNs. A variety of reaction conditions have been tested which include changing the base or solvent and comparing stirring vs sonicating. Table 2 summarizes the reaction conditions that have been tested. The most effective conditions so far have been using either NaOH or K_2CO_3 as the base while sonicating over night. Copper capacities (batch conditions: 1500 ppm, pH 2) of 0.100 mmol/g have been achieved for PAA-CSMNs and 0.200 mmol/g for PEI-CSMNs. In the next quarter, reaction conditions will further be optimized and adapted to large-scale (40g) production of CSMNs.

Table. 2. Summary of reaction conditions for functionalization of amines with carboxylic acid groups

Surface Polymer	Base	Solvent	Method
PAA	NaOH	Water	Stirring
PAA	Triethylamine	Water	Stirring
PAA	Triethylamine	Acetone	Stirring
PAA	NaOH	Water	Sonication
PEI	NaOH	Water	Sonication
PAA	K_2CO_3	Water	Sonication
PEI	K_2CO_3	Water	Sonication

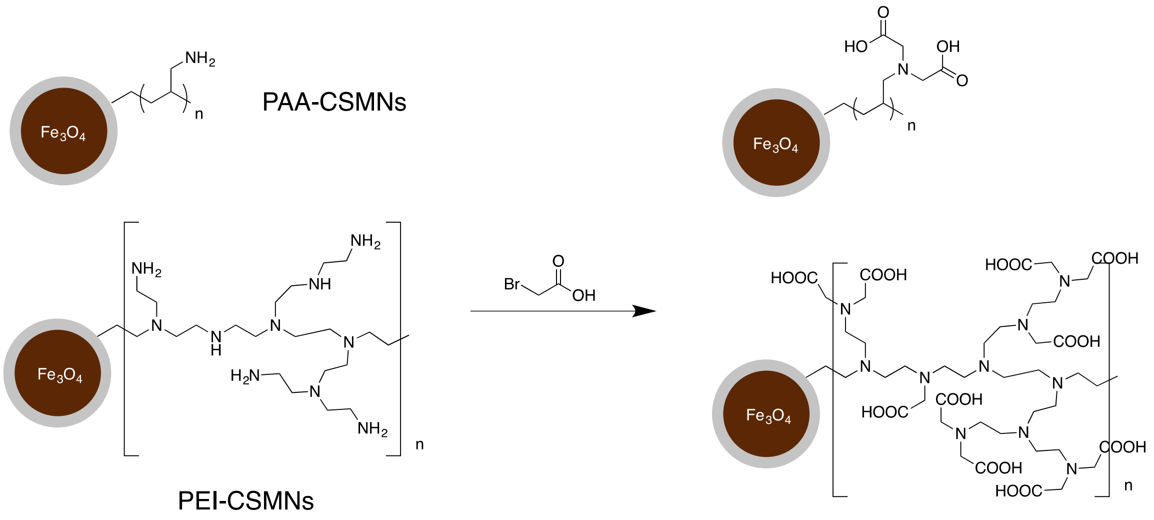


Figure 4. General reaction scheme for functionalizing CSMNs with carboxylic acid groups.

Summary of Progress (January 1 2017 – March 31 2017)

- Successful scale up to 40g of polyethylenimine CSMNs with reasonable copper capacities of 0.200 mmol/g
- Successful small-scale production of CSMNs that are able to capture metals at low pH.
- Investigated an alternate (although more expensive) source of aqueous nanoparticles that have been shown to produce greater copper capacities than current source of nanoparticles

Next Steps (April 1 2017 – June 30 2017)

- Large-scale (40g) synthesis of CSMNs with carboxylic acid ligands for metal capture at low pH (~2)
- Small and large-scale production of CSMNs with metal-selective ligands
- Continue to supply MTECH with CSMNs to be used in the flow reactor

A summary of the entire project to date:

1) We have produced two versions of CSMNs with different polymer structures (PEI and PAA) that have shown to have significantly different metal capture characteristics and different suspension properties.
2) We have, on the gram-scale, produced CSMNs which are able to capture metals at low pH.
3) We have been able to synthesize nanoparticles at a scale that is appropriate for the current flow reactor design.
4) We have identified the most effective starting point for synthesis is using a commercial source of iron oxide magnetic nanoparticles (Sky Spring Nanomaterials). We believe we have so far met our Key Milestones relating to Objective to #2.

OBJECTIVE 3: SECURE FUNDAMENTAL AQUEOUS PROCESSING DATA AND GENERATE PROCESS MODELS

MTECH TEAM; H.H. Huang (Co-PI)

Fundamental study: Adsorption reaction for ion exchanger made from fine silica gel particles

1. Introduction

Ion exchange research studies are normally divided in two different categories: the column experiments (which were discussed in the previous quarterly report) and batch experiments. Column tests are performed for the purpose of designing the operation, while batch tests examine variables that may influence not only the chemistry but also kinetics of the exchange reaction.

2. An Example

A batch study example published by Professor Rosenberg [1] is cited to understand the chemistry of the exchange reaction. The exchanger, the contaminants and variables are:

- Resin (Exchanger) – Phosphonic acid modified nanoporous modified silica gel with immobilized Zr(IV)
- Contaminants (ions to be removed) – As(V) and As(III)
- Variables: pH = -log{H+} and ratios Zr/P, As/P and As/Zr.

The effect of each variable was investigated by holding others constant. The study showed that a maximum adsorption of arsenate occurs at pH = 4. By using the Eh-pH diagram, Professor Rosenberg concluded that H_2AsO4^- (one of arsenate species) is the most likely species to be adsorbed by the exchanger. This conclusion is supported by the high ratio of As/Zr = 1.2 (the higher the better). Other pHs and species would have a lower ratio. For instance at pH 6, As/Zr could only be 0.8.

The same paper also indicated that the adsorption follows the Langmuir isotherm which is one of the commonly used models to describe from batch experiments. See the listings below.

3. Adsorption models

Several mathematical models have been used to formulate the exchange reaction from batch tests. They are divided into two main groups depending on the equilibrium or the kinetics point of view.

3.1 Equilibrium models

Using q_e for adsorption density inside the exchanger at equilibrium, and C_e is equilibrium concentration in the solution phase, equations are:

1) Langmuir adsorption equation where K_L and a_L are Langmuir constants

$$q_e = \frac{K_L C_e}{1 + a_L C_e}$$

2) Freundlich adsorption equation where K_F and A_F are Freundlich constants

$$q_e = K_F C_e^{A_F}$$

3.2. Kinetic models (Reference 2). Again q_e is used for adsorption density at equilibrium. The adsorption q_t at a given time t can be formulated by the following 3 models. Equations are:

1. Pseudo first order reaction where k_1 being the first order rate constant,

$$ln(q_e - q_t) = ln(q_e) - k_1 t$$

2. Pseudo second order reaction where k_2 being the seconder order rate constant,

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t$$

3. Elovich model where a and b are constants,

$$q_t = \frac{1}{b} ln(ab) + \frac{1}{b} ln(t)$$

OBJECTIVE 4: CONTINUOUS FLOW REACTOR DESIGN, CONSTRUCTION, COMMISSIONING, AND OPERATION.

MTECH TEAM; Jerry Downey (PI), David Hutchins.

In the 6th quarter, the fourth generation continuous flow reactor was designed and constructed. Data generated from experimentation with the third generation reactor were utilized to overcome issues encountered due to particle agglomeration and settling. A constant head, gravity fed vertical column reactor was devised, as shown in Figure 5.

Figure 5. The Fourth Generation Continuous Flow Reactor System. Solution flows down through the vertical column from the head tank to the PVC wye. The electromagnet is seated near the top of the PVC wye.

- 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. During operation, magnetic particle collection occurs within the novel wye module.
- The Wye module incorporates a water-cooled electromagnetic coil with density separation. The wye utilizes an innovative union system allowing for inspection and cleaning.
- Specialized static mixer components were developed to achieve ample contact and mixing. Design and additive manufacturing of the components was performed in-house.
- Experiments have confirmed operating parameters such as flow and particle collection efficiency.
- Design and procurement of a glass reactor was initiated. The design is nearly identical to the existing polymeric reactor, and will function in tandem. The glass construction will allow for visual inspection of the process and will increase durability and cleanability.

A series of experiments was conducted with surrogate solutions in order to model mixing within the reactor. Copper sulfate solutions of various concentrations were introduced into the reactor and the effluent was sampled at specific intervals. The samples were analyzed via ICP-AES and a model was developed to serve as the baseline for comparison in future experiments.

Experiments with ion-exchange particles provided by Dr. Rosenberg have been initiated. Surrogate ionic solutions at concentrations typical of local mine affected waters have been run with an appropriate mass of particles. Samples of the effluent and the concentrate are analyzed via ICP-AES and are awaiting interpretation. Experimentation will continue in order to define optimum process operating parameters and to secure process design criteria. In addition, experiments with samples collected from the Berkeley Pit and other local mine waters have been initiated.

Peripheral experimentation has continued:

- Metal recovery technologies continue to be explored. Parameters for electrowinning of copper are being optimized; results to date indicate that coherent copper cathode can be produced with starting solutions with copper tenors as low as 1 g/L. Similarly, the lower limits of zinc electrowinning are being established. Product samples have been generated and await characterization.
- Experiments with manganese electrowinning are ongoing. A manganese electrowinning cell has been designed and constructed, and commissioning of the cell is underway.
- Parameters for the stripping and regeneration of the particles are being established. Supernatant solution samples from the process are being analyzed via ICP-AES and the data will be included in the mass balance.
- Automation of the system nears completion. A graphical user interface is now capable of controlling all components including pumps, valves, and electromagnets. Data logging of pH, temperature and other parameters has been demonstrated.
- Detailed three dimensional plans of the reactor are being drafted.

During the past quarter, Christina Eggensperger performed research (discussed below) under the direction of Katherine Zodrow to investigate two potential causes for enhanced particle aggregation in the reactor: pH and ionic strength

<u>Effect of pH on Particle Aggregation</u>

- A Malvern Zetasizer was used to measure zeta potential and particle size. Zeta potential is an indication of particle surface charge, and particles with the same charge (positive or negative) tend to repel each other. Likewise, particles of opposite surface charge (i.e. positive and negative) or of neutral charge tend to agglomerate. Zeta potential is dependent upon the pH of the solution and generally decreases with increasing pH, depending on the functional groups present.
- For each condition, zeta potential was measured 50 times using a refractive index of 2.42. The pH of the sample was adjusted by adding 0.05 M HCl or NaOH. Samples were sonicated to achieve a good particle dispersion.
- Both magnetite core particles and modified (Reli-89) particles were measured.
- Magnetite core particles have a point of zero charge (PZC) at pH ~3. Thus, at pH ~3, magnetite particles will have a net neutral surface charge (Figure 6A). This neutral surface charge leads to aggregation at and near that pH, as is evident given the higher particle size measurement near pH 3 (Figure 6B). At higher pH, particle sizes are relatively small. All measurements at pH > 6, indicated a particle diameter of 603 ± 252 nm, while the highest particle size (measured at pH 3.2) was 4300 nm.
- Because the adsorbent particles used in the reactor are surface modified, they display different surface charge characteristics, and have a PZC of pH ~7 (Figure 6C). Thus, we predict that pH will not have much of an effect on particle stability in the reactor (operating at pH 4). However, it is important to note the wide spread in the data gathered, and some samples measured near pH 4 did have near zero zeta potential.
- Because the Reli-89 particles were much larger than the magnetite cores, we were not able to obtain reliable size measurements using the Zetasizer.

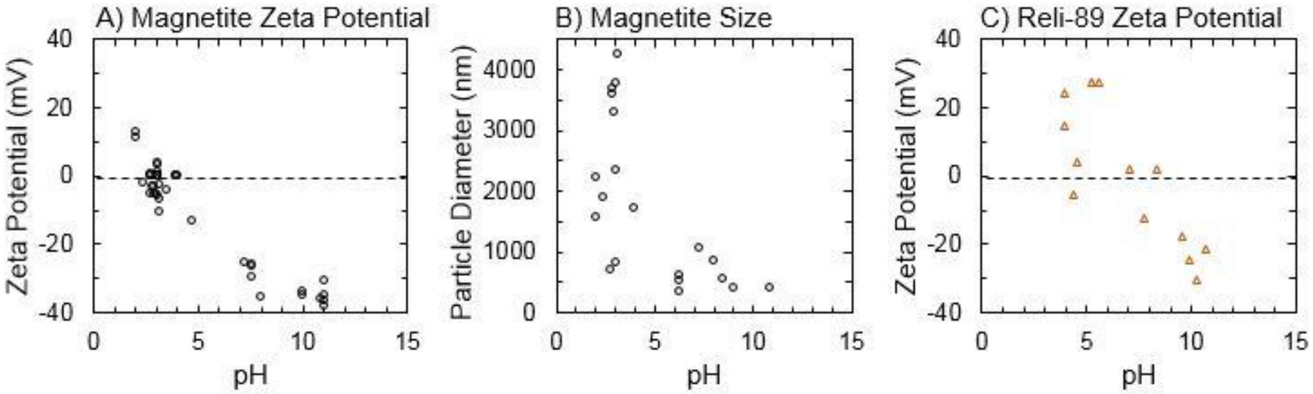


Figure 6. Influence of pH on particle zeta potential and size: (A) zeta potential of magnetite cores; (B) magnetite core size; and (C) Reli-89 zeta potential. The dotted line on (A) and (C) indicates zero zeta potential.

Effect of Ionic Strength on Particle Aggregation

- Ionic strength can also impact particle stability. Charged particles have ions of the opposite charge on their surface. If the ions on the surface of the particle do not completely negate the charge of the particle, then a cloud of ions of the opposite charge will exist around the particle. This cloud of oppositely charged ions, the electric double layer, contributes to particle stability (as like charges repel). However, in solutions of high ionic strength, the double layer thickness decreases, decreasing particle stability. We hypothesized that the high copper concentrations in the reactor will lead to electric double-layer compression and particle instability.

- Because of the large particle size, the Zetasizer could not be used to measure the influence of ionic strength on particle aggregation. Therefore, we used UV-vis spectroscopy to measure the absorbance (at 600 nm) in the bulk suspension. A solution of stable particles will have a higher absorbance than a solution of unstable particles, which tend to aggregate and settle to the bottom.

- Suspensions of Reli-89 particles at equal concentrations were made in water with different concentrations of sodium chloride (NaCl). The NaCl concentrations were chosen to mimic the ionic strength of the copper sulfate ($CuSO_4$) in the reactor. For example, 500 mg/L $CuSO_4$ has the same ionic strength as 0.0125 M NaCl. NaCl concentrations were varied from 0 to 0.05 M, and the absorbance over 10 min was observed. While similar aggregation rates were observed for ionic strengths of 0 to 0.025 M NaCl, higher ionic strengths, especially 0.05 M NaCl, led to faster aggregation rates. This indicates that high ionic strength may lead to decreased particle stability and increased particle aggregation, which could potentially prove a problem for reactor operation, depending upon the ionic strength inside the reactor.

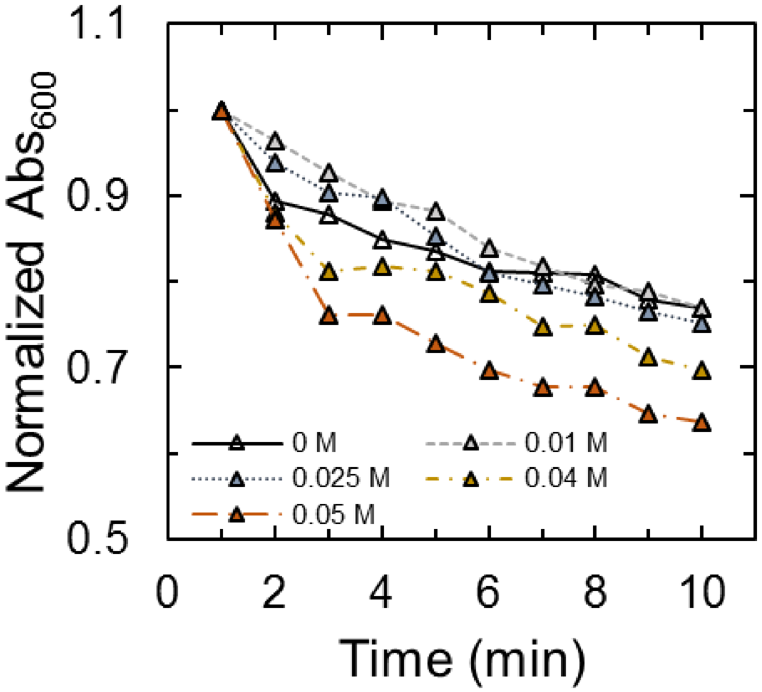


Figure 7. Stability of Reli-89 particles at different ionic strengths.

OBJECTIVE 5: DATA CONSOLIDATION AND REPORTING

- Documentation protocols, including laboratory notebook, file naming and sharing procedures, have been established and are in effect.
- The established project metadata accumulation, consolidation, and security measures remain in effect.

REFERENCES

1. V. Kailasam, E. Rosenberg, and D. Nielsen, "Characterization of Surface-Bond Zr(IV) and Its Application to Removal of As(V) and As(III) from Aqueous System Using Phosphonic Acid Modified Nanoporous Silica Polyamine Composites," *Ind. Eng. Chem. Res*., **2009**, 48, pp 3991-4001.

2. T.M. Zewail and N.S. Yousef, "Kinetic study of Heavy metal ions removal by ion exchange in batch conical air spouted ben," *Alexandria Engr. J.*, **2015**, 54, pp 83-90.