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

October 1 to December 31, 2016

Prepared by:

Jerome Downey, Professor, Montana Tech Department of Metallurgical and Materials Engineering (PI)

Edward Rosenberg, Professor, The University of Montana Department of Chemistry & Biochemistry (PI)

Hsin Huang, Professor, Montana Tech Department of Metallurgical and Materials Engineering (Co-PI)

Alysia Cox, Assistant Professor, Montana Tech Department of Chemistry and Geochemistry (Co-PI)

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

This quarterly progress report covers the project period from October 1, 2016 to December 31, 2016. 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. The team rosters are:

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

- David Hutchins, Materials Science Ph.D. student at MTech

- Jared Geer, undergraduate student in M&ME at MTech

- Renee Schmidt, Geochemistry M.S. student at MTech

- Maureen Chorney, M&ME M.S. student at MTech

- Auva Speiser, undergraduate student in Metallurgical and Materials Engineering at MTech

- Elizabeth Raiha, undergraduate student in M&ME at MTech

UM TEAM; Ed Rosenberg, PI

- Ryan Latterman, Post-Doctoral Research Associate

- Two undergraduate students

EXPENDITURES

Total expenditures of $229,561 were recorded through the end of December, 2016, representing approximately 46% of the overall project budget of $495,127. The rate of expenditure was lower than anticipated because procurement of equipment necessary to construct the 4th generation reactor at MTech was deferred to the next quarter (January 1 through March 31, 2017) in order to allow time to modify the reactor design in light of recent findings. All phases of the project remain within budget.

Table 1 – Summary of Project Expenditures through December 31, 2016*

Category	Budget	Amt Spent	% Spent	Balance
Personal Services	$ 162,226	$ 104,287	64.3	$ 57,939
Contracted Services				
Subcontracts	$ 188,001	$ 98,725	52.5	$ 89,276
General	$ 50,000		0.0	$ 50,000
Supplies	$ 45,000	$ 20,476	45.5	$ 24,524
Travel	$ 2,500	$ 44	1.7	$ 2,456
Utilities	$ -	$ 202		$ (202)
Other	$ -	$ 25		$ (25)
Waivers & Scholarships	$ 17,400	$ 5,803	33.3	$ 11,597
Capital Equipment	$ 30,000	$ -	0.0	$ 30,000
Total Operating & Capital	**$ 495,127**	**$ 229,561**	**46.4**	**$ 265,566**

***totals do not include expenditures that did not enter the accounting system before December 31.**

MTECH TEAM

- Total Budget: $307,126; total expenditures of $131,055 (42.7%) through December 31, 2016.

- Expenditures for Supplies and General Contracted Services (specifically analytical support) are anticipated to surge in the next quarter as the focus of the research transitions from reactor design and development to experimental determination of metal removal efficiencies.

- The entire capital equipment budget ($30,000) is projected to be consumed during the next quarter. Equipment procurement was deferred to this point because the MTech team wanted to confirm the modified reactor design before committing funds to the acquisition of the new equipment.

UM TEAM

- Total Budget: $188,001; total expenditures of $98,506 (52.4%) through November 30, 2016.

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

PROGRESS TOWARD MILESTONES

In the following sections, progress is described according to the specific project objectives.

OBJECTIVE 1: WASTEWATER CHARACTERIZATION

MTECH TEAM; Alysia Cox (Co-PI)

- The Laboratory Exploring Geobiochemical Engineering and Natural Dynamics (LEGEND) has sampled local surface waters on five different days (5 sites per day) for a total of 25 samples sites since the beginning of the project. 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).

- We have graphed GWIC data of rare earth element concentrations in the flooded mine shafts, to assess recovery potential (see Figure 1).

- Renee Schmidt received the 2nd Place Student Poster Award at the Montana American Water Resources Association (AWRA) Meeting held Oct. 13-14th at the Fairmont Hot Springs Resort. The conference focused on "Water Quality & Quantity in a Changing Climate" and Renee's poster detailed geochemical changes in flooded mine shafts.

- Schmidt presented a talk on geochemical changes in flooded mine shafts at the 2016 Mining and Mineral Symposium held at the MBMG on October 21st on campus. Her abstract will be published.

- Schmidt presented a poster about geochemical changes in flooded mine shafts at the American Geophysical Union Fall Meeting in San Francisco last week, December 11-16. Her abstract is in press.
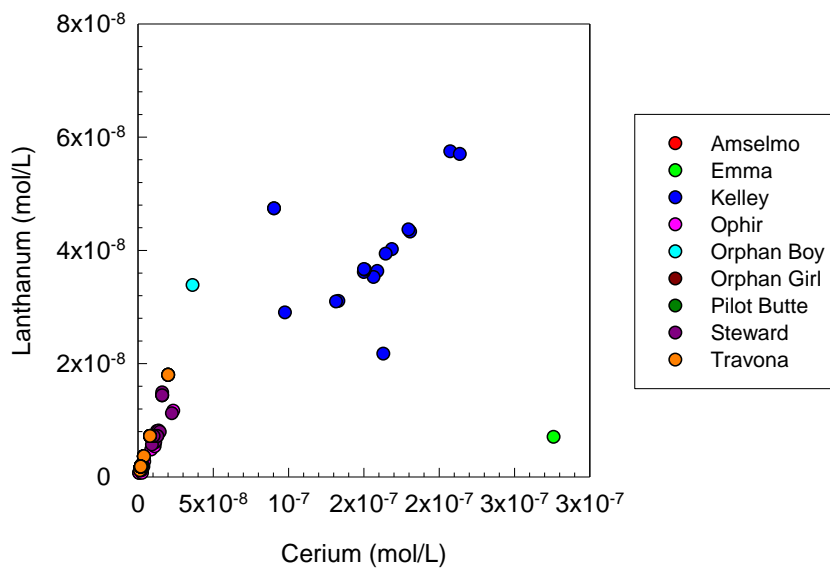

Figure 1: Lanthanum vs. Cerium in nine flooded mine shafts.

OBJECTIVE 2: MAGNETIC NANOCOMPOSITE SYNTHESIS

UM TEAM; Ed Rosenberg (PI)

Synthesis and characterization iron-magnetic nanoparticles modified for metal ion capture.

1. **Further scale up to 40 grams using commercial source of magnetite nanoparticles**

A significant goal of this past quarter involved scaling the synthesis of core shell magnetic nanoparticles (CSMNs) up to 40g while also obtaining acceptable copper capacities. At first, the target of 0.500 mmol/g Cu^{2+} could not be achieved at the larger scale. Initially, we tried increasing the reaction times and amount of poly(allylamine) (PAA) polymer but this was not successful. Eventually, it became obvious that the PAA most recently purchased is much less effective than our older supply of PAA. At the moment, the reasons are unclear especially since we are using the same product number and supplier. We then investigated how changing the molecular weight and source of a variety of PAA polymers affected the copper capacity of the nanoparticles. At the moment, the most effective route to 0.500 mmol/g is using a 60,000 molecular weight PAA polymer while also increasing the reaction time to 24 hours and using 5 mL of PAA solution per gram of CSMNs. Previously, the reaction conditions called for a 3 hour reaction using 1 mL of PAA solution per gram of CSMNs. Table 1 shows a summary of results using different PAA polymers. Polysciences, Inc. also has available a 150,000 molecular weight PAA which we will be trying in future experiments.

Table 1. Copper capacities of iron oxide CSMNs using various PAA polymers.

Source of PAA	Molecular Weight	Cu Capacity (mmol/g)
Nittobo (Old Bottle)	15,000	0.450 to 0.550
Nittobo	15,000	0.200 to 0.300
Nittobo	3000	0.200 to 0.300
Polysciences	15,000	0.200 to 0.300
Polysciences	60,000	0.400 to 0.500

2. **Stripping and Reuse Studies of CSMNs functionalized with 3,000 and 60,000 molecular weight PAA**

After investigating the copper capacities while varying molecular weight of PAA, we wanted to verify whether the molecular weight of the PAA affected the copper stripping and reusability of the CSMNs. To perform one cycle, 100 mg of CSMNs were mixed with 10 mL of 1200 ppm Cu^{2+} (via $CuSO_4$ at intrinsic pH) in a 15 mL centrifuge tube and sonicated for 1 minute in a bath sonicator. Because previous kinetics studies showed extremely fast capture rate, the CSMNs were left to equilibrate for an additional 9 minutes after sonication for a total of 10 minutes of equilibrium time. CSMNs were then collected using a permanent magnet and a dilution was prepared for Atomic Absorption analysis before discarding the supernatant. After one 10 mL wash with water, the CSMNs were left in contact with 10 mL 0.1M citric acid for two minutes, washed once with 10 mL water, left in contact with 10 mL of 1 M ammonium hydroxide for 2 minutes, washed once more with 10 mL of water and finally one time with 5

mL of acetone and dried with a stream of air before the addition of more Cu^{2+} at the start of a new cycle. All cycles were performed in triplicate for each NP sample. Figure 2 shows the copper capacities through 4 cycles comparing CSMNs functionalized with 3,000 MW to CSMNs with 60,000 MW PAA. (Note: the 60,000 MW sample only had a copper capacity of 0.328 mmol/g as it was a sample made before optimizing the reaction time and polymer concentration.)
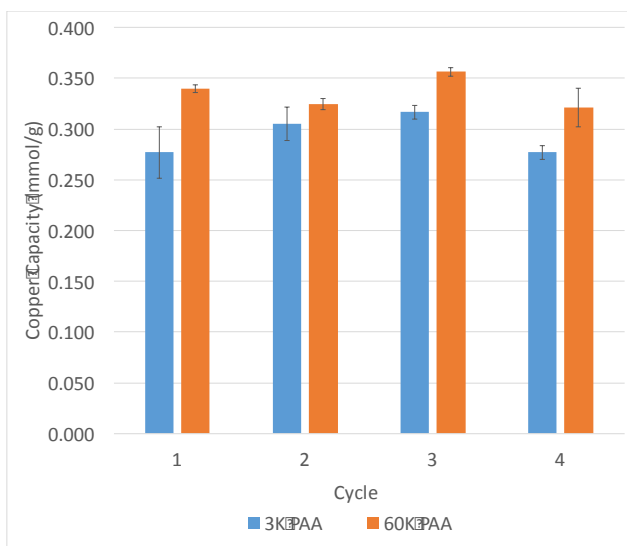

Figure 2. Copper capacities of CSMNs functionalized with 3,000 and 60,000 MW PAA. Each cycle indicates the copper capacity after CSMNs are subjected to both stripping (citric acid) and regeneration (ammonium hydroxide) solutions.

Figure 3 shows the copper capacities through eleven reuse cycles of the 60,000 MW PAA sample. At cycle 11, a small drop in capacity is observed which may be contributed to particle loss from incomplete collection on the permanent magnet during wash steps. The data observed for both NP samples is encouraging. We have confirmed that under fairly mild conditions and fast equilibrium times, copper can be stripped and the CSMNs can be reused for up to eleven cycles. Additional studies will be performed in the next quarter that will establish the optimal volume of both the stripping reagent (citric acid) and regeneration reagent (ammonium hydroxide) in order to minimizing chemicals used in the process.
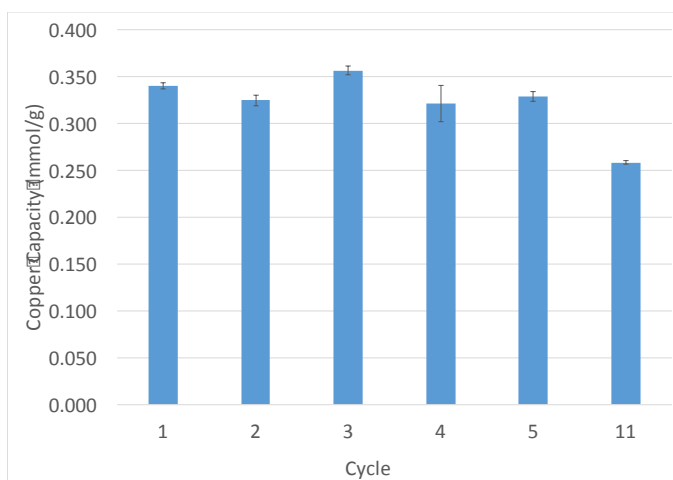

Figure 3. Copper capacities of CSMNs functionalized with 60,000 MW PAA through 11 strip and reuse cycles.

3. Size analysis of commercial vs lab-made one-component CSMNs via Dynamic Light Scattering

In the previous quarterly report, we noted that we had been investigating a new method of synthesizing magnetite nanoparticles that used a one-component system rather than the co-precipitation of two iron salts. This new method uses very simple synthesis conditions and, at the small scale, produces CSMNs that are more easily dispersed in water compared to the commercial particles that we have been using as surrogates in the flow reactor at MTECH. At the ~7 g scale, we were able to achieve copper capacities between 0.550 and 0.700 mmol/g. However, after repeated attempts scaling up to 20 g, we were unable to achieve these capacities. We hypothesized that the particle size produced at the large scale must be significantly different than when producing the same particles at a smaller scale. Using dynamic light scattering (DLS), we confirmed this suspicion. Table 2 shows the z-average diameters of CSMNs produced using the new one-component synthesis at small and large scales. The z-average diameter of the large scale particles is almost double that of the small scale. After discussing our strategy with our collaborators at MTECH, we are going to focus on large scale synthesis using commercial magnetite nanoparticles going forward.

Table 2. DLS data of CSMNs. The large Z-average diameter reflects agglomerates of nanoparticles after being coated in both silica and PAA polymer. We believe the large size difference between small and large scale lab-made one-component CSMNs is contributing to the difference in copper capacities.

CSMN Sample	Z-average (nm)	Copper Capacity (mmol/g	Reference Number
Commercial (Silica Coated + PAA)	602	0.500	REL1_114
Small Scale One-Component (Silica Coated + PAA)	533	0.500 to 0.700	REL1_103
Large Scale One-Component (Silica Coated + PAA)	903	0.200	REL1_77

4. Summary of Progress

- Successful scale up to 40g with reasonable copper capacities of 0.500 mmol/g

- CSMNs have been shown to be useful for metal capture after 11 cycles of copper stripping and regeneration

- Confirmation using DLS that a 20g scale up of lab made one-component magnetite synthesis is producing much larger sizes and subsequently less copper capacity. At the moment, this focuses our efforts further towards using commercially available iron oxide CSMNs.

5. Next Steps

- Large scale (40g) synthesis of CSMNs with aminoacetate ligands for metal capture at low pH (~2)

- Optimize volume of stripping and regeneration solutions for reuse cycles

- Increase scale of reuse cycles

- Continue to supply MTECH with CSMNs to be used in the flow reactor

- Minimize aggregation by using detergent prior to modification

- Measure particle size at each step of synthesis to see degree of aggregation

- TEM and SEM at each step of synthesis

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

Most ion exchange (IX) operations use a packed bed column. The mass, M, of the resin required depends not only on the solution flow rate (Q) and concentration (C_o) but also the resin's capacity to extract (q_o) and the kinetics constant of exchange reaction (k_1). The breakthrough curve is one of the key factors for the design of the column. It starts at the time (or volume of solution introduced) when metal (or pollutant) starts to leak out of the column until the exchanger in the column is totally exhausted. A typical breakthrough curve is illustrated in Figure 4; in the figure, MTZ stands for mass transfer zone where the active adsorption reaction is taking place.
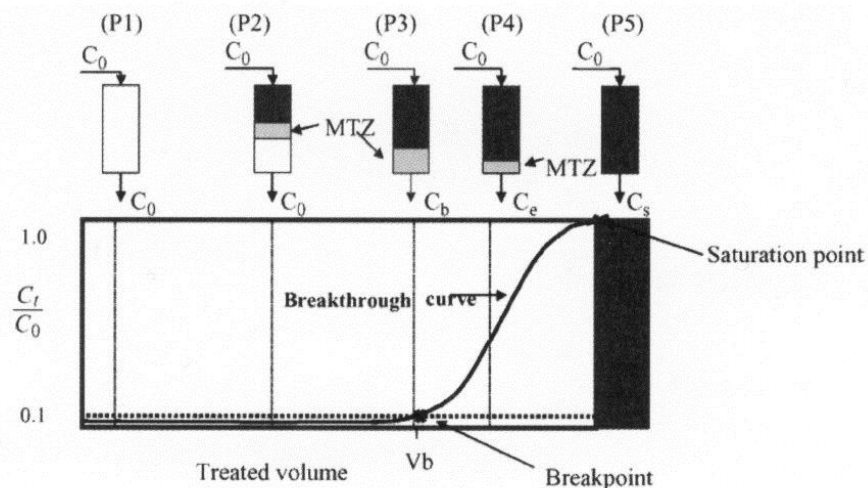

Figure 4. Typical breakthrough curve from an ion exchanger column operation [1]

2. Formulating the Breakthrough Curve – Thomas Model

The Thomas model [2] is one of the commonly cited mathematical equations to formulate the breakthrough curve. The equation is simple and expressed for the concentration ratio between input (C_o) and output (C_t) as a function of time (t) or total volume introduced (V). Other parameters include exchanger capacity (q_o) and kinetics constant (k_1), and conditions to operate: weight of exchanger (M) and solution flow rate (Q).

$$\ln\left(\frac{C_o}{C_t} - 1\right) = \frac{k_1 q_o M}{Q} - \frac{k_1 C_o V}{Q} \text{ where } V = Q \times t \qquad\qquad \text{EQ1}$$

Data from Adsorption of Ca^{2+} by Amberlite IRC 748 from K_2CrO_4 aqueous solution are used for brief demonstration [3]

2.1 Estimating exchange capacity q_o and k_1 from experimental data

The capacity and the kinetics constant can be evaluated from the breakthrough curves obtained experimentally. According to Equation 1, a linear relationship between $\ln(C_o/C_t - 1)$ and V (or t) can be observed (see Figure 5). Parameters, q_o and k_1, can be computed from the slope $= - k_1 C_o/Q$, and intercept $= k_1 q_o M/Q$ of the straight lines.

2.2 Predicting the Breakthrough Curve for given Conditions

Once the exchange capacity and rate constant are obtained, the breakthrough curves versus volume flow rate (or time) can be computed using Equation 2 (derived from Equation1). The operation conditions such as the influent concentration, (C_o), mass of exchanger (M) and solution flow rate Q can be varied and implemented to the equation. Experimental data and model prediction under 3 different Ca^{2+} concentrations taken from Reference 3 are shown on Figure 6.

$$\frac{C_t}{C_o} = \frac{1}{\left(1 + \exp\left(\frac{k_1 q_o M}{Q} - \frac{k_1 C_o V}{Q}\right)\right)} \qquad\qquad \text{EQ2}$$

2.3 Design for the operation

The design of column is normally concentrated on total amount of resin needed for getting $C_t/C_o = 5\%$ (or 10%) from the breakthrough curve. The curve is constructed by including all other conditions required to operate the system.
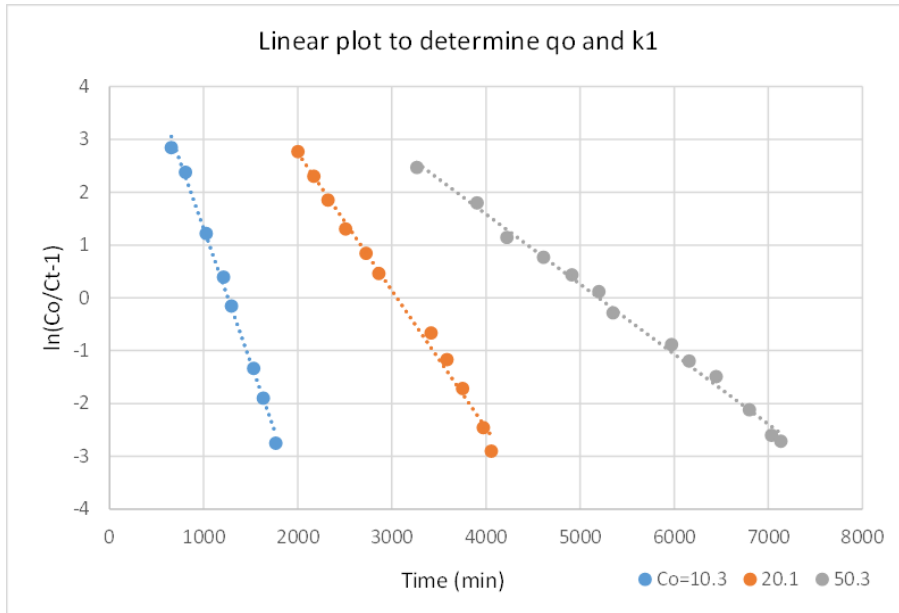
Figure 5: Linear plot to estimate exchange capacity, q_o and kinetic constant, k_1.
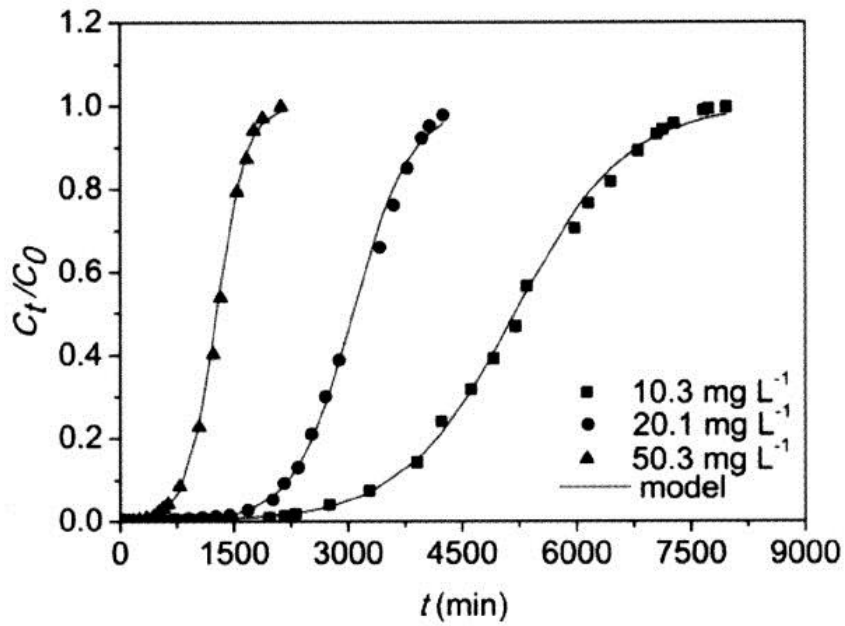

Figure 6: The model predicted the breakthrough curves versus points from 3 different experiments

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

MTECH TEAM; Jerry Downey (PI), David Hutchins

Experimentation with the continuous flow reactor and electrowinning cell continued in the 5th quarter.

- Improved magnetic collection modules were designed and built. These modules incorporate a clamshell design that allows for easy inspection, cleaning, and modification. The latest coil design has demonstrated improved magnetic flux density and collection efficiency. One of the modules is depicted in Figure 7.

- Efforts to automate the operation and data collection have continued. A graphical user interface shown in Figure 8 was designed for control of all aspects of the process. Calibration of the temperature, pH, electrical, and flow sensors was conducted. Safety measures were incorporated to eliminate the possibility of overheating.

- Experiments were conducted with the coated particles in the bench-scale reactor. Challenges with particle agglomeration were identified, and a revised reactor design is being undertaken. It is expected that the fourth reactor design iteration will be completed and functional in January of 2017.

- Arrangements were made with the Montana Bureau of Mines and Geology to secure samples of water from the Berkeley Pit for testing in the reactor. Sampling is planned for early January.

- Experimentation with the electrowinning cell continues. Lower limits of copper concentration have been established, and coherent copper sheets have been produced from (surrogate) starting solution with copper tenors of less than 1 gram per liter. Design of alternate cells for other target metals has been initiated.

- An NSF-STTR proposal was submitted in partnership with a local engineering firm. This proposal focused on the potential of the technology in the removal and recovery of selenium from industrial waste waters. The total Phase 1 is $224,996 with $134,996 intended for university research and the balance for research to be performed by the industrial partner.

- Jerry Downey accepted an invitation to deliver a project-related presentation at Recycling Metals from Industrial Waste short course and workshop, which will be held at Colorado School of Mines, June 27-29, 2017.

  Activities for the upcoming quarter are expected to focus on commissioning and operation of the 4th generation flow reactor with emphasis on securing metal recovery

data. The metal recovery experiments will initiate with surrogate solutions and eventually move to recovery of metal from the actual mine wastewater samples.

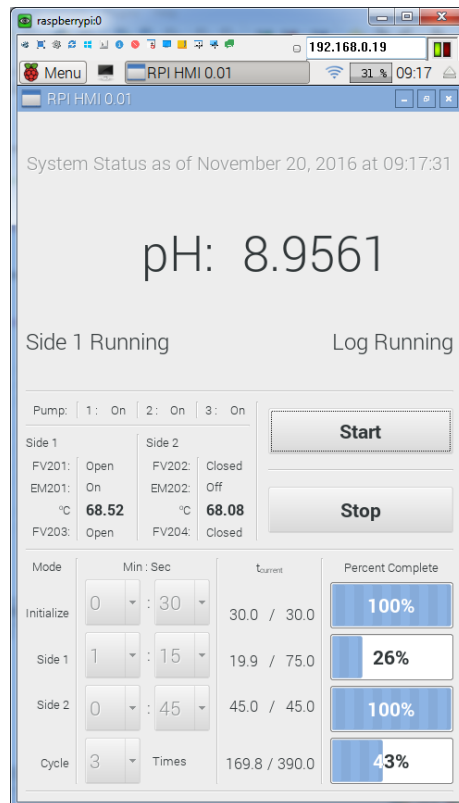**Figure 7. Flow Reactor Graphical User Interface**

Figure 8. Flow Reactor Graphical User Interface

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. G. Tochobanoglous et al., Wastewater Engineering, Treatment, Disposal and Reuse, McGraw-Hill, New York, 1991

2. H.C. Thomas, Heterogeneous ion exchange in a flowing system, J. Am. Chem. Soc. 66, 1664-1666 (1944)

3. Z. Yu, et al., Application of mathematical models for ion-exchange removal of calcium ions from potassium chromate solutions by Amberlite IRC 748 resin in a continuous fixed bed column, Hydrometallurgy, 158 165-171 (2015)