ORNL/TM-2022/2604
CRADA/ NFE-18-07313

CRADA Final Report: CRADA Number NFE-18-07313 with Nth Cycle, Inc.

Megan O'Connor

Date: August 19, 2022

OAK RIDGE NATIONAL LABORATORY
MANAGED BY UT-BATTELLE FOR THE US DEPARTMENT OF ENERGY

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Division or Program Name

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1. Abstract

Cooperative Research and Development Agreement (CRADA) NFE-18-07313 between Oak Ridge National Laboratory (ORNL) and Nth Cycle Inc. focused on developing a technology for sustainable recycling of rare earth and specialty metals (e.g., Y, Co, Li; RESE), as well as bulk and precious metals from industrial manufacturing and waste streams through the use of electrochemical carbon nanotube-enabled filters. The project outcome was expected to be a stronger mechanistic understanding of the electrochemical recovery of metals from real manufacturing process streams and e-waste streams, and the development of an optimized high-throughput pilot-scale device ready for commercialization. Testing, design, and development of a v1 prototype to prove the technology was unsuccessful (we were not able to reach the go/no-go outlined in Objective 1) and we were unable to continue our redesign due to COVID-19 lockdown and no access to lab from March 2020 – until our graduation from the program.

2. Statement of Objectives

The four objectives of the CRADA, and their relevant tasks:

1. **Develop and test the pilot scale device to identify all performance issues, as well as assess economic viability needed for commercialization.**

   The pilot scale system will be built and tested with synthetic mixed metal waste streams. Experiments (Objective 2) will be used to assess the economic viability of the membrane as well as identify any performance issues that arise. We anticipate multiple iterations will be needed to achieve ≥ 50% recovery and 85% purity. This work will be completed by Nth Cycle and PI Paul Taylor.

   Task 1.1. *Build pilot scale apparatus*
   In this task, Nth Cycle will collaborate with PIs to build the pilot-scale device. Appropriate geometries and footprint of the device will be determined by volume of waste or processing streams and application (i.e., manufacturing recycling or end-of-life recycling).
   Preliminary benchmarks have been set for technology performance and economic viability, which include % recovery and selectivity. The recovery goal set here is 50%, or in other words, at least 50% of the starting material in the synthetic waste stream must be captured on the membrane. Selectivity is defined as the ability to separate metals from each other (i.e., the ability to separate the bulk and precious metals from each other, and to separate bulk and precious metals from RESE). Here, we have set the selectivity threshold at ≥ 85% purity for each separated metal. Note: The objective is to separate bulk and precious metals from RESE, and collect RESE as a "mixed cake". This mixed cake of RESE has been determined to be valuable to manufacturers through personal

communications with electronic companies. The specific experiments to determine these benchmarks for each filter are explained in detail in objective 3, which will be completed in parallel to this objective.

2. **Test the device with synthetic and real manufacturing/e-waste streams as a function of system parameters to evaluate process efficiency and to enhance the mechanistic understanding of recovery from mixed metal streams.**

Single and specific mixed metal streams (i.e., synthetic metal streams of interest to industry, such as NdFeB, LiCoNi, etc.), as well as e-waste and manufacturing streams (i.e., acid digested magnets, batteries, and shredded HDDs) will be tested across the specified parameter space to identify and optimize the settings needed for maximum separation and capture. This work will be completed by Nth Cycle and PIs Tim McIntyre and Bruce Moyer.

Task 2.1. *Optimize process parameters for electrochemical precipitation in scaled devices*

(1) *Flow Rate.* We seek to determine the influence of flow rate on metal recovery. The first goal is to establish a flow rate where adequate recovery (i.e., 50% or greater) is achieved. Here, I will test the metals with a range of flow rates from 1 - 20 L/hour. Secondarily, we seek to determine the maximum possible flow rate our filters can handle while maintaining high recovery rates and avoiding system pressure issues (e.g., leaking or filter breakage).

(2+3) *Voltage and pH.* The main goal of this subtask is to identify a unique range of voltages and pH for each metal (i.e., a voltage and pH that is sufficient to overcome the reduction potential of one or a few metals, but not all), to reach the selectivity benchmark of $\geq$ 85%. To do this, I will measure the recovery for a variety of metals over a range of voltages from 0 – 3.5 V at 0.1-0.5 V intervals and pH from 0 – 10 at the optimized flow rate from (1).

(4) *Concentration.* Here, we seek to identify the mass limitation of our CNT membrane. I will run synthetic waste streams across the flow rate range and calculate mass flux and molar flux. This will help assess the number of membranes needed for a particular waste stream. This subtask will be run in combination with (1).

Task 2.2. *Digest and run e-waste through system at optimized parameters*

In this task, Nth Cycle will obtain samples from PI and digest and test the separated e-waste components including but not limited to magnets, batteries, and hard drives. These components will be digested in a mix of hydrochloric and nitric acid (and titrated to neutral pH if needed) and then passed through the device at the optimized parameters from Task 3.1.

3. **Investigate solid- and liquid- based methods to remove metals off the membranes after high recovery is achieved to determine membrane reusability and metal reuse in advanced manufacturing.**

   Solid- and liquid- based techniques such as mechanical scraping and acid rinsing will be investigated to determine the best method to retrieve these metals off the CNT membrane. Additionally, membrane reusability or recycling will also be tested through repeat recovery experiments to identify material limitations. This work will be completed by Nth Cycle, and PIs Tim McIntyre and Paul Taylor.

Task 3.1. *Test recovery methods in scaled devices for metal reuse*

This objective is to determine how recovered metals can be effectively removed from the CNT membranes for use or reuse in advanced manufacturing. Here, we will test both solid- and liquid- based methods. These include mechanical scraping, combustion of the membranes, and acid flushing. If the metals are depositing solely on the surface, mechanical scraping should be efficient (e.g., if sufficient material is collected on the top surface of the filters and mechanical integrity of the filter allows repeated scraping events). In contrast, metals deposited on interior filter surfaces (e.g., on the internal surface of the membrane but outer surface of the CNTs) may require acidic flushing or total combustion of the membrane in order to recover the metals. Here, we aim to identify the most effective method to recover these metals off the CNT membranes to produce usable material for industrial manufacturing, exploring the effect of acid concentration and counter ion choice, as well as total combustion approaches. These experiments will be run in the scaled devices from objective 2.

Task 3.2. *Determine membrane reusability*

After each recovery method is tested, repeat initial metal capture experiments with optimized parameters from objective 3 and recovery off the membrane methods will be completed to determine the membrane reusability.

Reusability will be measured by the same benchmarks outlined in objective 2, ≥ 50% recovery and selectivity ≥ 85%.

4. **Determine the devices's ability to separate individual RESE**
Task 4.1. *Digest and run e-waste through system to separate RESE*

In this task, Nth Cycle will digest and test the separated e-waste components and manufacturing waste streams and identify the optimum parameters for RESE separation and recovery in the system, as well as develop a chemical separation step if needed. This objective will also be performed in parallel to Objective 2 and 3, testing the synthetic streams of mixed RESE across the parameter matrices outlined in Task 3.1. We anticipate multiple iterations will be needed between the synthetic and real waste streams as information is gathered and parameter space is narrowed. This work will be completed by Nth Cycle and PI Bruce Moyer.

The set benchmarks for technological performance and economic viability are similar to those in Objective 2, with a higher purity standard set for individual RESE here. The recovery goal set here is 50%, or in other words, at least 50% of the starting material in the e-waste stream must be captured on the membrane. Selectivity is defined as the ability to separate metals from each other (i.e., the ability to separate the RESE metals from each other). Here, we have set the selectivity threshold at ≥ 90% purity for each separated metal. Further chemical methods to separate these metals after recovery will be developed and tested as the technology matures.

3. Benefits to the Funding DOE Office's Mission

A new, cleaner technology to refine metals will enhance the sustainability of the industries core to the electrification movement, helping to secure the supply of critical materials for the Federal Government for clean energy development expansion. Additionally, it will give incentive to industry and consumers to recycle instead of mine primary materials. Further, the technology will provide the first in-stream separation capability for electronic and semiconductor manufacturers enabling them to eliminate losses of RESE in processing streams, maximizing atom economy and minimizing material costs.

4. Technical Discussion of Work Performed by All Parties

This is a report based on the work performed in the aforementioned task list.

Task 1.1 involved designing a pilot scale system for the technology. For the design to meet the threshold to move on to other tasks was a recovery of 50% or great, or in other words, at least 50% of the starting material in the synthetic waste stream must be captured on the membrane. The v1 system that we designed and constructed can be seen in Figure 1.

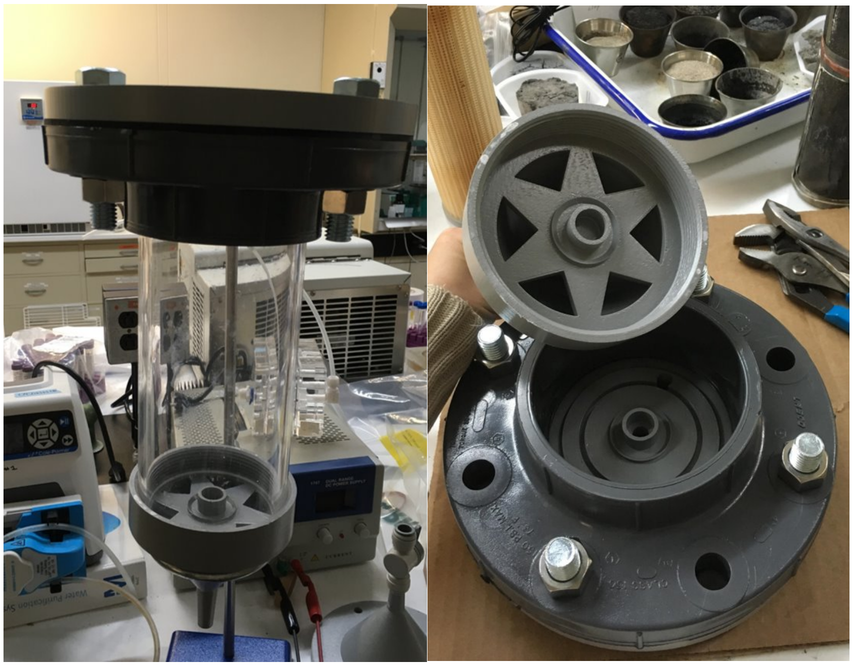

Figure 1. v1 system

Through the many rounds of design iterations, we ran into issues with leaking, clogging, and low current efficiency. We worked with the PIs to trouble shoot these issues and came up with the design in Figure 1. After that system was assembled, we proceeded to test with synthetic metal salts. To start these tests, we used neodymium chloride. As you'll see in Figure 2 and Table 1, we could see neodymium oxide being captured on the carbon nanotube membrane (The white particles shown in Figure 2), but the recovery was very low (10% at best; Table 1).

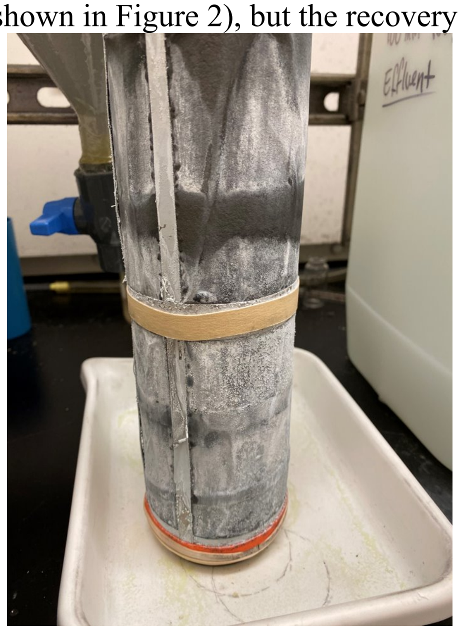

Figure 2. v1 design tested with synthetic neodymium

	Nd	Nd	Nd
	Absorption	Concentration [mM]	Percent Recovered [%]
Starting Jug	0.240054846	34.28	
2 V	0.230299488	32.89	4.06
3 V	0.234140962	33.44	2.46
4 V	0.220670492	31.51	8.07
5 V	0.215585232	30.79	10.19
6 V	0.223044753	31.85	7.09
7 V	0.232510373	33.20	3.14
8 V	0.236796215	33.82	1.36
9 V	0.236489371	33.77	1.49

Table 1. UV-vis data for the neodymium study

These tests indicated that there was a leak somewhere in the system or that the electrical contacts were not in the proper place.

Task 1.1 took much longer than anticipated and we were not able to reach this point until December 2019. In January 2020 we started to redesign this system to engineer out the failure points, but could not complete the rest of the objectives due to COVID-19.

5. Subject Inventions (As defined in the CRADA)

None.

6. Commercialization Possibilities

The results from the v1 system demonstrated low recovery of neodymium. Even with these learnings from the v1 system, we were unable to build a system that could yield the recovery we need to make the system economically viable for neodymium. As a result, Nth Cycle started looking at the battery metals after we graduated from Innovation Crossroads.

7. Conclusions

During this CRADA, a v1 system for the electrochemical recovery of metals was developed, built, and tested with a synthetic stream rare earth metals. Other designs were being developed in early 2020 and as a result of COVID-19, we were unable to complete this task or move on to the other tasks.