# Environment and Natural Resources Trust Fund
# 2019 Request for Proposals (RFP)

**Project Title:** **ENRTF ID: 061-B**

Membranes for Removing Toxic Metals from Mining Wastewater

**Category:** B. Water Resources

**Sub-Category:**

**Total Project Budget: $** 449,203

**Proposed Project Time Period for the Funding Requested:** June 30, 2022 (3 yrs)

**Summary:**

We will develop, test, and implement new highly-selective membranes for the removal of toxic metals in mining wastewater treatment facilities to help ensure long-term safety of Minnesota mining operations.

**Name:** Marc Hillmyer

**Sponsoring Organization:** U of MN

**Title:** Professor

**Department:** College of Science and Engineering / Chemistry

**Address:** 207 Pleasant St SE

Minneapolis MN 55455

**Telephone Number:** (612) 625-7834

**Email** hillmyer@umn.edu

**Web Address** http://hillmyer.chem.umn.edu

**Location**

**Region:** Central, Northwest

**County Name:** Aitkin, Carlton, Cass, Crow Wing, St. Louis

**City / Township:**

**Alternate Text for Visual:**

An overview of how our new membrane technology fits into existing mining wastewater treatment processes.

| | | | |
|---|---|---|---|
| _____ Funding Priorities | _____ Multiple Benefits | _____ Outcomes | _____ Knowledge Base |
| _____ Extent of Impact | _____ Innovation | _____ Scientific/Tech Basis | _____ Urgency |
| _____ Capacity Readiness | _____ Leverage | _____ TOTAL | _____% |
| ____ If under $200,000, waive presentation? | | | |

**PROJECT TITLE: Membranes for Removing Toxic Metals from Mining Wastewater**

**I. PROJECT STATEMENT**

| |
|---|
| We will develop new polymeric membranes for treatment of mining wastewater to help ensure the long-term safety of mining operations in Minnesota. |

Toxic heavy metals such as lead, mercury, and cadmium are dissolved in effluent water that has been used for mining operations, and release of these metals into surface and ground waters is a major public health and environmental concern. Currently, water containing these toxic contaminants is treated on-site and stored in ponds near the mines, and some projections estimate that these operations will require monitoring for centuries to prevent the contaminated water from escaping into the environment. As mining continues to expand in Minnesota, the need for new technologies for more effective treatment of mining wastewater will become ever more important. **The development of alternative methods for the removal of toxic heavy metals from mining wastewater would greatly benefit Minnesota by helping to ensure the safety of valuable mining operations and the surrounding environment.**

Polymers – materials such as plastic and rubber – are used to produce many types of membranes. These materials are thin sheets that allow some chemicals to pass through while retaining others. Through chemical modification, their selectivity can be tailored for different applications. **We will develop polymer membranes that have selectivity for the toxic metal ions present in mining wastewater, thus allowing selective, low-cost, and low-energy purification of contaminated wastewater**. Currently, mining water treatment uses the membrane-based reverse osmosis process, which purifies water while retaining *nearly all* ions, including non-toxic species like sodium and calcium. Unfortunately, this process requires high pressure and thus large amounts of energy. In contrast, our ion-selective membranes will be designed to remove only toxic metal ions, using minimal energy and small amounts of benign chemicals. These membranes could be incorporated into the existing mining water treatment process to ensure discharged water is free of heavy metals and to decrease the heavy metal content in storage ponds. Additionally, valuable heavy metals can be reclaimed.

We will use our expertise in polymer synthesis and membrane fabrication to develop a family of new materials that can readily be modified to fit the specific characteristics and concerns of each mining site at which they are implemented. The membranes will be mechanically robust, chemically stable, and will result in the **removal of toxic metals from water to below state and federally-mandated limits**. The small amount of specialized polymer required for effective toxic metal removal will ensure a low overall cost of these new materials.

**II. PROJECT ACTIVITIES AND OUTCOMES**

**Activity 1: Synthesis of robust polymer membranes – ENRTF BUDGET: $179,682**

One of the primary challenges in the synthesis of polymer membranes is to develop a material that is thin enough for high permeability, but also exhibits mechanical stability such that it does not break under its operating conditions. One strategy to address this difficulty is the incorporation of so-called hard segments into the polymer, which lend toughness to the material. Our research group has recently developed a method by which one polymer – that allows metal ions to permeate through the material – can be easily bound to a second polymer, which lends mechanical robustness to the membrane. **In this way, a membrane can efficiently remove heavy metals while possessing a long operational lifetime**. Under this activity we will use this method to make thin membranes and optimize their performance for both permeability and stability. In addition, the polymer will require reactive sites that can be modified with metal-binding structures (see Activity 2), and identification of a suitable polymer which lends itself to membrane fabrication will be addressed in this Activity.

| Outcome | Completion Date |
|---|---|
| *1. Identification of polymers able to incorporate metal ion-binding sites* | *February 2020* |
| *2. Optimization of membrane fabrication process* | *April 2020* |

| | |
|---|---|
| *3. Investigation of factors that influence membrane performance* | *August 2020* |

**Activity 2: Modification of membranes for metal ion binding – ENRTF BUDGET: $89,840**

After successful synthesis and characterization of the membranes developed in Activity 1, metal-binding sites will be introduced within the membranes. Functionalization of the membranes in the solid state poses a challenge due to issues of kinetics and accessibility of the reactive sites. To overcome this challenge, we will employ reactions characterized by high yields, fast kinetics, and mild reaction conditions. Polymers identified in Activity 1 will be used to introduce metal binding sites. In addition, the use of distinct binding sites will provide the membranes with **tunable selectivity for use in varied environments depending on the primary toxic metal pollutants of concern, enabling their adoption at different mining sites.**

| Outcome | Completion Date |
|---|---|
| *1. Identify and test suitable metal-binding species for incorporation into membranes* | *December 2020* |
| *2. Optimize functionalization of membrane in the solid state* | *March 2021* |

**Activity 3: Testing and modeling membrane performance – ENRTF BUDGET: $179,682**

In this activity, membranes will be tested for their ability to rapidly and selectively remove toxic heavy metals from a mixed salt solution containing competing, non-toxic metal ions such as sodium and calcium. Membranes will be assessed in a diffusion cell, in which the membrane separates a metal-contaminated water solution from a metal-free strip solution. Authentic mining wastewater samples will also be used to demonstrate the ability of the membranes to function with real waste streams. This activity will enable fundamental characterization of transport behavior and assess how the behavior is affected by material properties, which will be used to **further optimize the membrane to maximize the effectiveness of the toxic water purification process.** Characterized parameters will also allow for the modeling of full-scale treatment processes, which will demonstrate the feasibility of the process for incorporation into existing onsite water treatment plants. We anticipate interaction with the UMN Natural Resources Research Institute during this phase of the research activity and have had preliminary discussions with Director Donald Fosnacht on related sustainability topics.

| Outcome | Completion Date |
|---|---|
| *1. Optimize use of membranes to remove heavy metals from artificial mining wastewater* | *July 2021* |
| *2. Demonstrate practical utility by treating real mining wastewater in lab-scale setup* | *January 2022* |
| *3. Model performance of an actual treatment process* | *May2022* |

**III. PROJECT PARTNERS:**

**A. Partners receiving ENRTF funding**

| | | | |
|---|---|---|---|
| Marc Hillmyer | Professor | Univeristy of Minnesota | Principal Investigator |

**B. Partners NOT receiving ENRTF funding: None**

**IV. LONG-TERM- IMPLEMENTATION AND FUNDING:**

The proposed work fits well into numerous efforts in the Hillmyer research group focused on development of novel membrane materials using the modern tools of chemistry. The expertise in the Hillmyer group will provide complementary expertise that will be very beneficial to the efforts proposed here.

**V. TIME LINE REQUIREMENTS:**

The project period is from June 2019 to May 2022. We will submit periodic project updates biannually. A final report will be submitted by the end of August 2022.

# 2019 Proposal Budget Spreadsheet

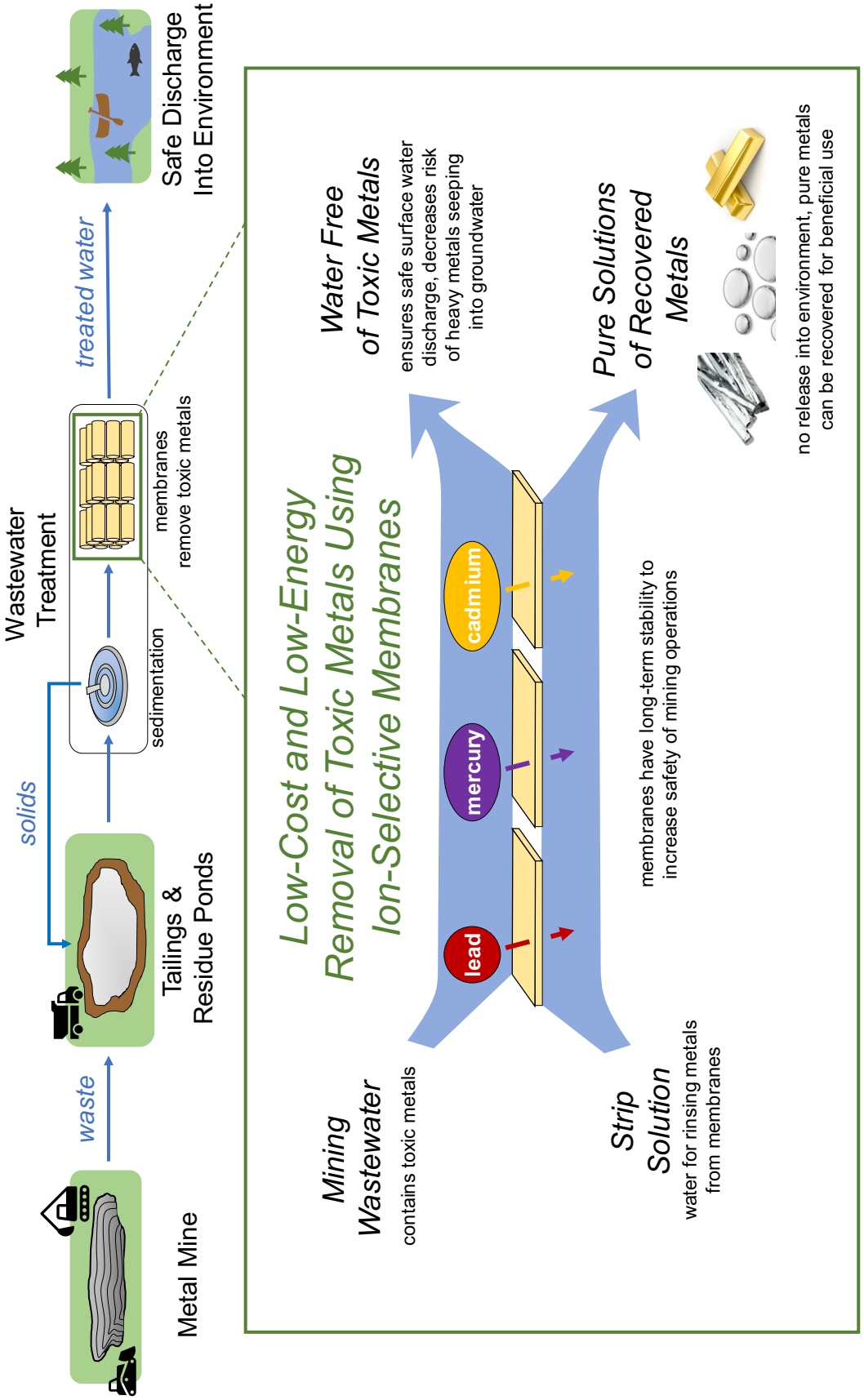
**Project Title: Development of Ion-Selective Membranes for Mining Wastewater Treatment**

**IV. TOTAL ENRTF REQUEST BUDGET** *3* **years**

| **BUDGET ITEM** (See "Guidance on Allowable Expenses") | **AMOUNT** |
|---|---|
| **Personnel: Principal Investigator. Professor. 74% of funds for salary, 26% of funds for fringe. 2 weeks during summer in each year of the project. This is approximately 4% of a 12-month appointment, but Professor's base appointment is only a 9-month term. One person in this position.** | $ 43,210 |
| **Personnel: Post-doctoral Associate. 82% of funds for salary, 18% of funds for fringe. This is 100% of a 12-month appointment in each year of the project. One person in this position.** | $ 183,341 |
| **Personnel: Graduate student. 46% of funds for salary, 44% of funds for fringe benefits, including tuition remission. This 50% (20 hours per week) for 12-months in each year of the project. One anticipated person in this position, though may share the work among multiple graduate students to total an average of 20 hours per week.** | $ 139,611 |
| **Professional/Technical/Service Contracts:** | $ - |
| **Equipment/Tools/Supplies:** Chemicals, glassware, lab supplies as needed for the project duration. This will include monomers, ligands, test diffusion cells, laboratory equipment, flasks, | $ 53,823 |
| **Acquisition (Fee Title or Permanent Easements):** | $ - |
| **Travel:** | $ - |
| **Additional Budget Items:** Scientific Services to include NMR spectroscopy; size-exclusion chromotography; transmission electron microscopy; small-angle x-ray scattering; dynamic mechanical analysis; and scanning electron microscopy need to characterize the membrane materials. | $ 29,218 |
| **TOTAL ENVIRONMENT AND NATURAL RESOURCES TRUST FUND $ REQUEST =** | $ 449,203 |

**V. OTHER FUNDS** *(This entire section must be filled out. Do not delete rows. Indicate "N/A" if row is not applicable.)*

| **SOURCE OF FUNDS** | **AMOUNT** | **Status** |
|---|---|---|
| **Other Non-State $ To Be Applied To Project During Project Period:** | N/A | |
| **Other State $ To Be Applied To Project During Project Period:** | N/A | |
| **In-kind Services To Be Applied To Project During Project Period:** There is no Univeristy of Minnesota overhead included in the budget. UMN facilities, electricity, laboratory space, and other infrastructure will be provided.We will also encourage capable undergraduates to apply for summer research fellowships to work on this project during the summer periods. | Standard UMN overhead costs are ~54% of the direct costs | |
| **Past and Current ENRTF Appropriation:** Prof. Hillmyer is a collaborator on a project led by Prof. Paige Novak entitled "Innovative Nitrogen Removal Technology to Protect Water Quality". Profs. Michael Tsapatsis and Romero Vargas Castrillon are also co-investigators. This was funded in FY2017-FY2018 (Proposal 04b-#034B) | $450,000 | |
| **Other Funding History:** | N/A | |


Safe Discharge Into Environment
treated water
Wastewater Treatment
membranes remove toxic metals
sedimentation
solids
Tailings & Residue Ponds
waste
Metal Mine
Low-Cost and Low-Energy Removal of Toxic Metals Using Ion-Selective Membranes
Water Free of Toxic Metals
ensures safe surface water discharge, decreases risk of heavy metals seeping into groundwater
Pure Solutions of Recovered Metals
no release into environment, pure metals can be recovered for beneficial use
Mining Wastewater
contains toxic metals
lead
mercury
cadmium
membranes have long-term stability to increase safety of mining operations
Strip Solution
water for rinsing metals from membranes

## *Marc Andrew Hillmyer*

*McKnight Presidential Endowed Chair, University of Minnesota*

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**EDUCATION**

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|---|---|
| Ph.D. Chemistry, California Institute of Technology | 1994 |
| B.S. Chemistry, University of Florida | 1989 |

**APPOINTMENTS**

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|---|---|
| College of Science and Engineering – University of Minnesota | |
| Director, Center for Sustainable Polymers | 2009–present |
| Department of Chemistry – University of Minnesota | |
| McKnight Presidential Endowed Chair | 2015–present |
| Distinguished University Teaching Professor | 2014–present |
| Distinguished McKnight University Professor | 2010–present |
| Professor | 2009–2010 |
| Elmore H. Northey Associate Professor, Professor | 2004–2007, 2007–2009 |
| Associate Professor | 2002–2004 |
| Assistant Professor | 1997–2002 |
| Department of Chemical Engineering and Materials Science – University of Minnesota | |
| Graduate Faculty Member | 1999–present |
| Postdoctoral Research Associate | 1994–1997 |

**HONORS**

| | |
|---|---|
| Entrepreneurial Researcher Award (UMN) | 2017 |
| McKnight Presidential Endowed Chair (UMN) | 2015 |
| NSF Division of Materials Research, Special Creativity Extension | 2014–2016 |
| Postbaccalaureate, Graduate, and Professional Education Award (UMN) | 2014 |
| PTN Medema Award | 2013 |
| LE STUDIUM research fellow, Université d'Orléans/CNRS | 2012–2013 |
| Fellow of the Polymer Chemistry (POLY) Division of the ACS | 2012 |
| Carl S. Marvel Creative Polymer Chemistry Award (POLY division of the ACS) | 2011 |
| Distinguished McKnight University Professorship (UMN) | 2010 |
| IonE Fellow (UMN) | 2010 |
| George W. Taylor/IT Alumni Society Award for Distinguished Teaching (UMN) | 2010 |
| Fellow of the American Association for the Advancement of Science (AAAS) | 2009 |
| Visiting Professor, Université d'Orléans, France | 2008 |
| Arthur K. Doolittle Award (jointly awarded, PMSE division of the ACS) | 2007 |
| George Taylor Distinguished Research Award (UMN) | 2007 |
| Leverhulme Visiting Professor, University of Cambridge | 2005–2006 |
| Best Chemistry Instructor Award (UMN Institute of Technology Student Board) | 2005 |
| Elmore H. Northey Professorship (UMN) | 2004–2009 |
| George Taylor Career Development Award (UMN) | 2002 |
| National Science Foundation CAREER Award | 2001–2005 |
| Packard Fellowship for Science and Engineering | 2000–2005 |
| Schlumberger Limited Foundation Award | 2000, 2001 |
| Camille Dreyfus Teacher-Scholar Award | 2000–2005 |
| McKnight Land-Grant Professorship (UMN) | 2000–2002 |
| DuPont Young Professor Grant | 1999–2001 |
| Research Corporation Research Innovation Award | 1998–2001 |
| 3M Company Non-tenured Faculty Award | 1998–2002 |
| IBM Graduate Research Fellowship | 1992 |
| American Institute of Chemists Student Award | 1989 |
| President's Recognition Award (UF); College Scholar Award (UF); Summerville Fellowship in Chemistry (UF) | 1989 |