Focused on the **Future**

NRRI Today and Tomorrow

Natural Resources Research Institute

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Developing Technologies for Mitigating Sulfate in Minnesota's Waters

Lucinda B Johnson
Sr. Research Fellow

Natural Resources Research Institute
University of Minnesota Duluth
Driven to Discover

Sulfate Team

- Dr. Lucinda Johnson
- Dr. George Hudak

Chemical Precipitation

- Dr. Meijun Cai
- Mr. Shashi Rao
- Dr. Adrian Hanson*
- Ms. Sara Post
- Mr. Matt Anthony

Peat Sorption

- Dr. Igor Kolomitsyn
- Dr. Sergiy Yemets
- American Peat Technology*

Biological

- Dr. ChanLan Chun
- Dr. Matthew Berens
- Dr. Nate Johnson*
- Dr. Randy Kolka*
- Dr. Lee Penn*

- PostDocs, students, interns, facility support staff

* Collaborator

Natural Resources Research Institute
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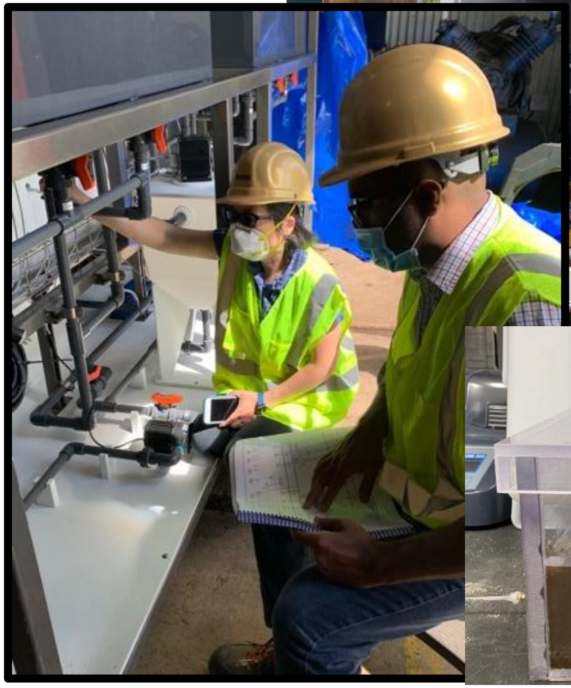
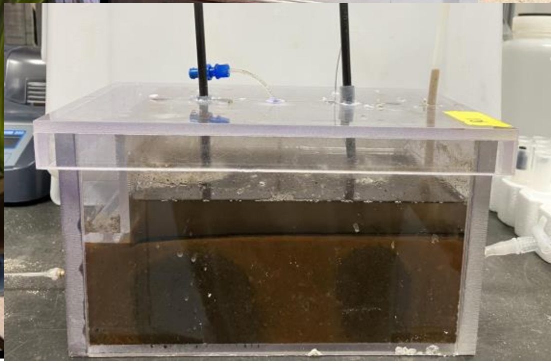
Outline

- NRRI Introduction
- Introduction to sulfate as a nutrient and pollutant
- Minnesota’s sulfate standard for wild rice waters
- Need for multiple remediation technologies
- NRRI – led technology solutions
    - Anion Exchange
    - Chemical Precipitation
    - Biological systems
- Summary / Discussion





NRRI Role

NRRI MISSION:

Deliver integrated research solutions

that value our resources, environment and economy for a sustainable and resilient future.

NRRI VISION:

Discover the Economy of the Future

Integrated Research • Innovative Science
Global Relevance

NRRI Expertise

Integrated Research Platforms

1. Applied Ecology and Resource Management
2. Minerals and Metallurgy
3. Materials and Bioeconomy
4. Data Collection and Delivery
5. Commercialization Services

NRRI Delivery

Strategic Initiatives

Future Forest Industries

Iron & Minerals of the Future

Ecosystem Resilience

Innovation Impacts

NRRI: Unique Integrated Capabilities

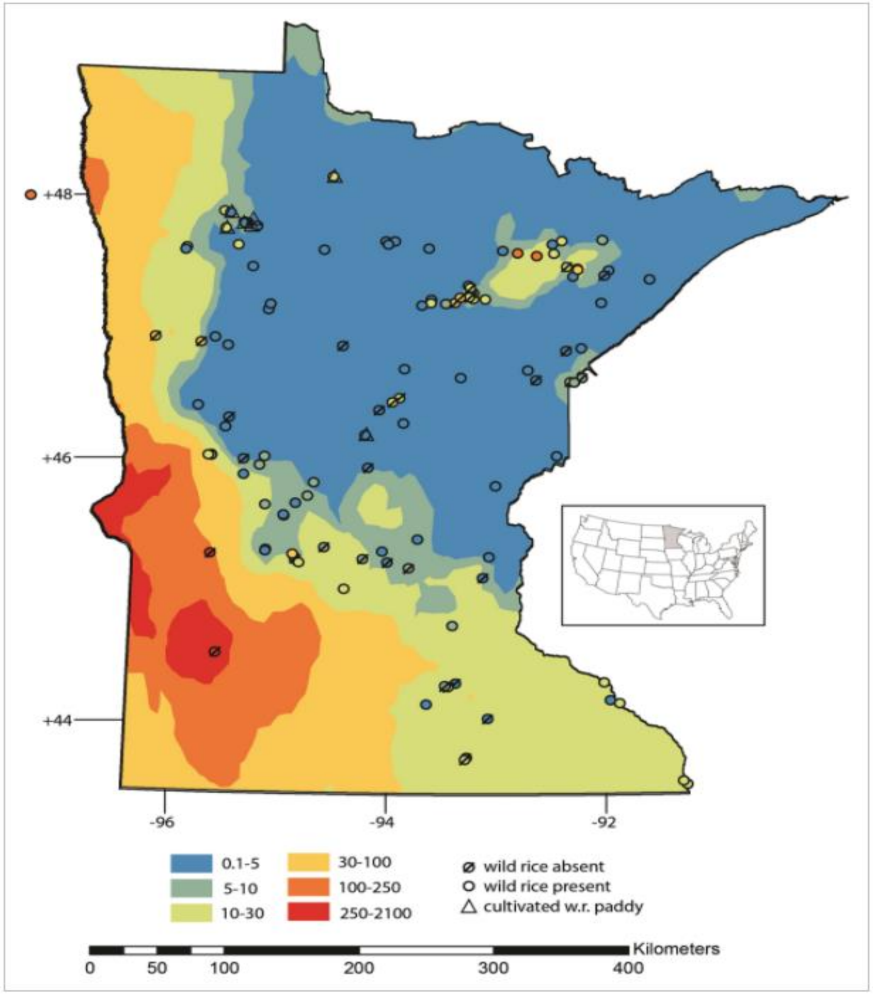
NRRI DULUTH

19 research labs and pilot areas for land and water ecosystem studies, wildlife, forestry, forest products, minerals, materials development and testing, and process development.

NRRI COLERAINE

15 building, 27-acre industrial lab site focused on minerals characterization, minerals processing, metallurgy, biomass processing, energy and materials research.

Sulfate in Minnesota



- Naturally low sulfate concentrations in northeast Minnesota

- Sources:
  - Rock weathering
  - Agriculture
  - Industrial wastewater
  - Consumer products

A. Myrbo, E. B. Swain ,D. R. Engstrom, J. Coleman Wasik, J. Brenner, M. Dykhuizen Shore,E. B. Peters,G. Blaha (2017), Sulfide Generated by Sulfate Reduction is a Primary Controller of the Occurrence of Wild Rice (Zizania palustris) in Shallow Aquatic Ecosystems. Journal of Geophysical Research: Biogeosciences.

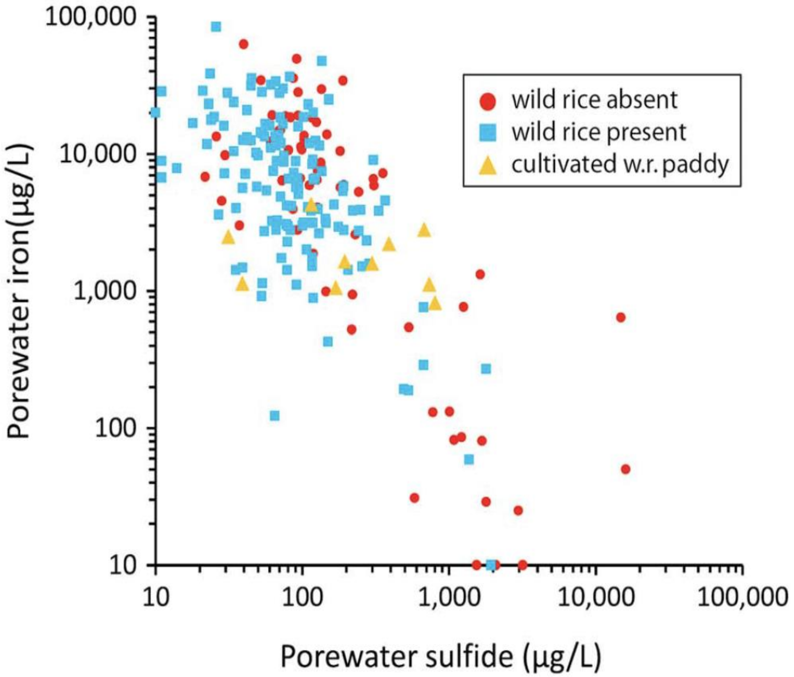
Sulfate is an essential nutrient.

- Influences buffering capacity of water body
- Enhances internal cycling of nutrients such as phosphorus
- Associated with biological mercury methylation
- Adverse impact on aquatic organisms above threshold levels

Excessive loads of sulfate may impact ecosystem and public health.

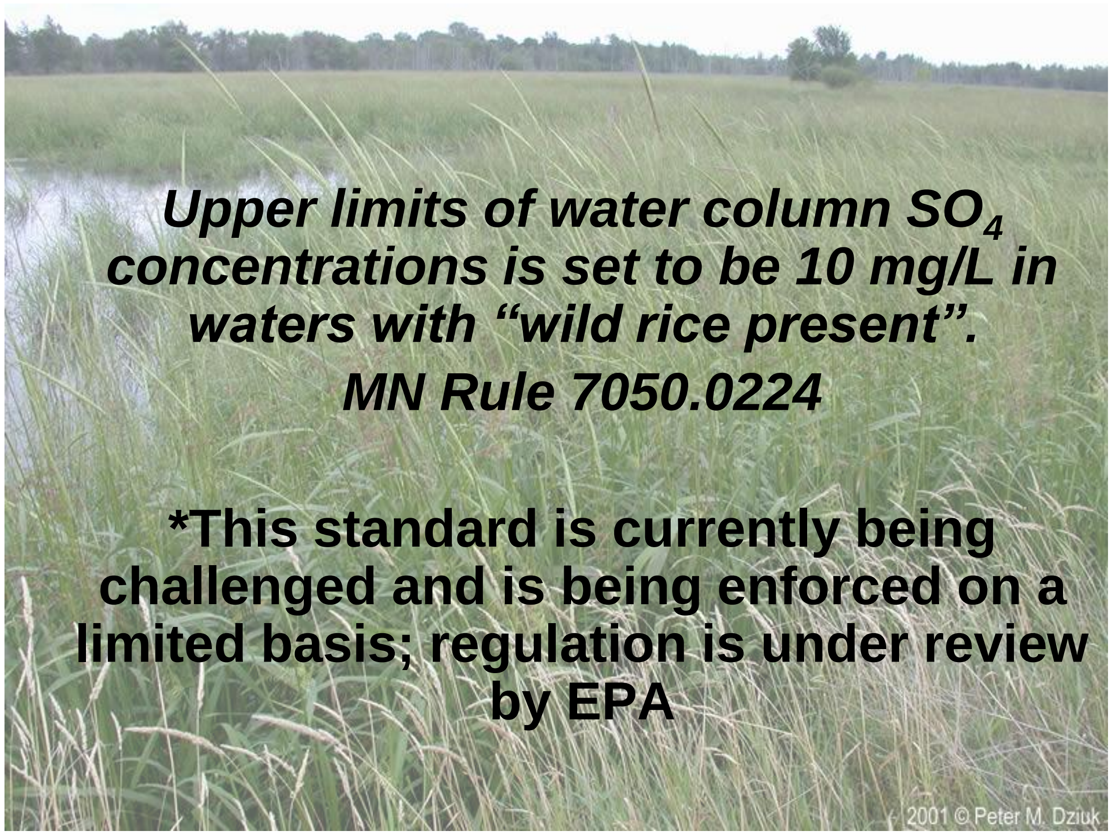
Background

- Empirical studies observed that wild rice populations were most robust when wate column sulfate concentrations were < 10 mg/L and did not occur when concentrations were > 50 mg/L (Moyle 1944)
- In the presence of **excess sulfide** there i a delay in reproductive phenology and a **decrease in N uptake** to seeds (LaFond-Hudson et. al. 2020)
- Recent field and laboratory studies show these phenomena are complicated by:
  - Hydrology
  - Organic Carbon
  - Iron concentration



Myrbo et al. 2017

Minnesota's Regulatory Sulfate Standard for Wild Rice Waters

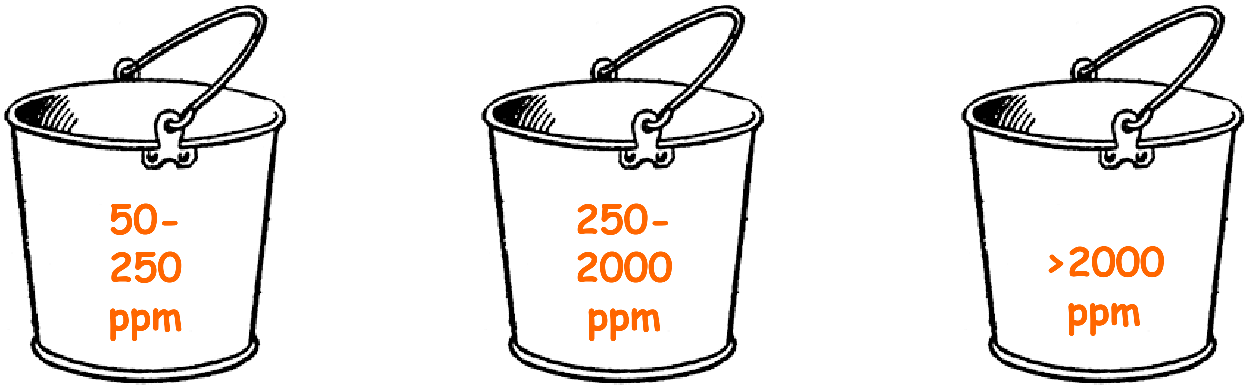


Upper limits of water column SO_4 concentrations is set to be 10 mg/L in waters with "wild rice present".

MN Rule 7050.0224

***This standard is currently being challenged and is being enforced on a limited basis; regulation is under review by EPA**

Sulfate Treatment: Three Regimes

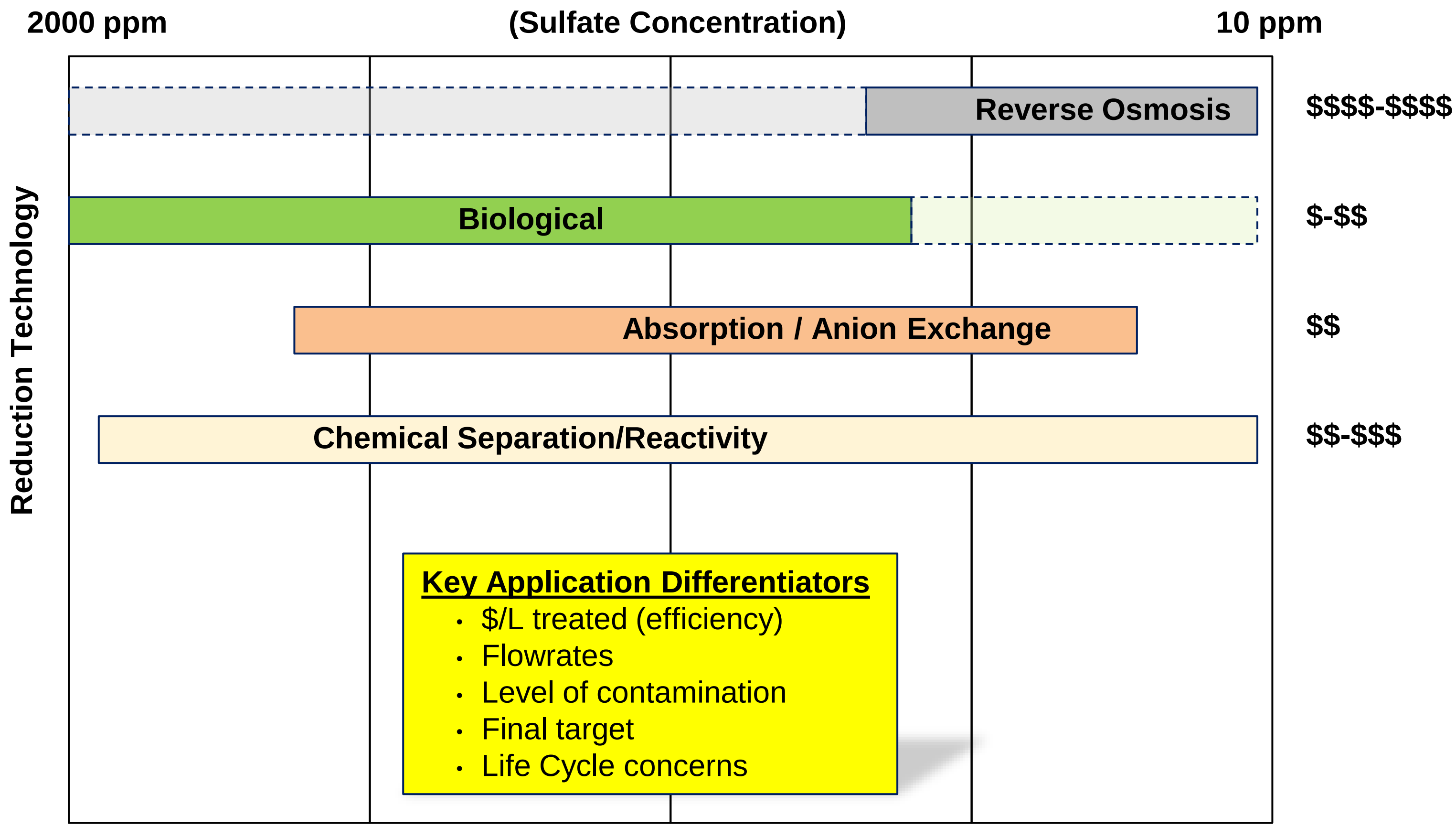


Municipal water treatment facilities	Agriculture, Industry, Mining Pit Lakes	Power Generation Effluent Treatment

Each individual challenge may require portfolio of two or more technologies applied in combination

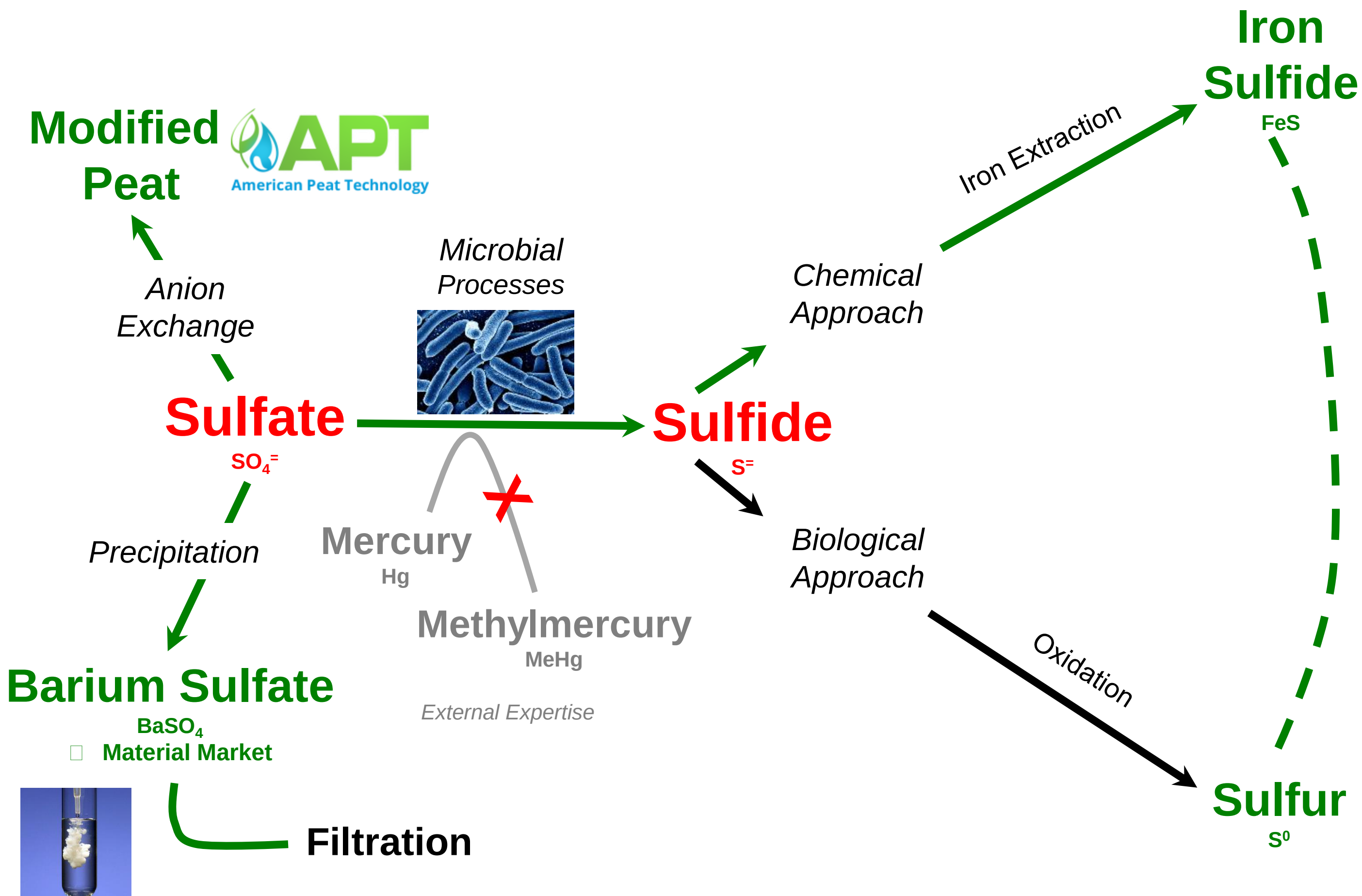
Sulfate Treatment Options

Example of Sulfate Reduction Technology Portfolio



It is essential to develop technologies to remediate sulfate in a cost-effective and efficient manner.

NRRI Waterborne Sulfate Reduction Programs



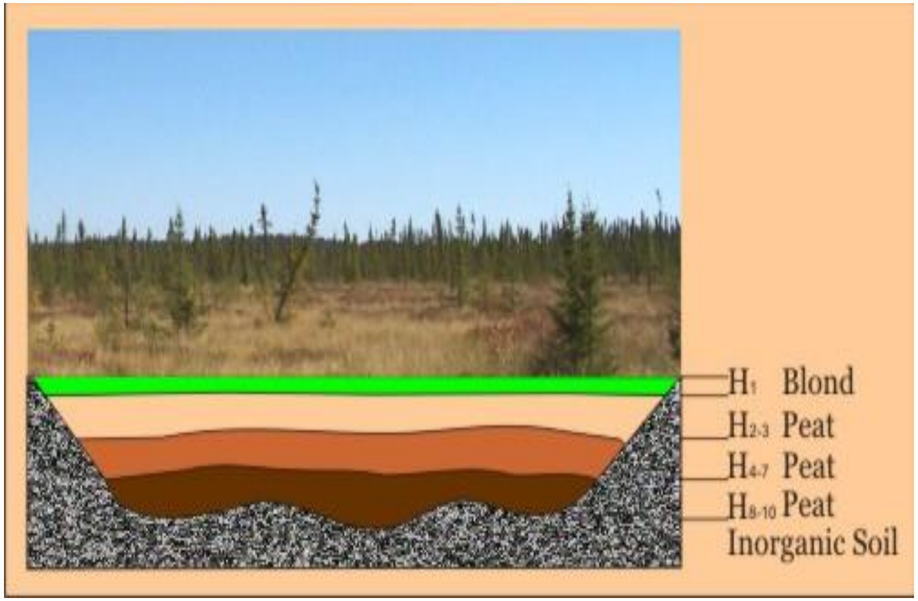
[Technology platforms also applicable to phosphate, selenate remediation]

Novel Materials Team

- Dr. Igor Kolomitsyn
- Dr. Sergiy Yemets
- American Peat Technology (collaborators)

American Peat Technology

Peat is a natural product formed largely from the inhibited decomposition of plant materials.[1]



[1] Morita, H., Peat and its organic chemistry. *Journal of Chemical Education* **1980,** 57, (10), 695-6.

Characteristics of ***natural*** peat*

- Has natural ability to absorb heavy metals
- Ion-exchange (capacity is 30 - 200 meq/100 g)
- Low mechanical strength
- High affinity for water
- Poor chemical stability
- Tendency to shrink and/or swell
- Leaching organic compounds
- Leaching heavy metal ions

Blue – good
Red - bad

* Brown, P. A.; Gill, S. A.; Allen, S. J., Metal removal from wastewater using peat. *Water Research* ***2000,*** *34, (16), 3907-3916.*

Value added natural peat-based products to treat mine and wastewater.

Technology

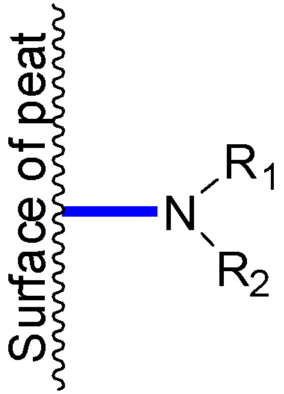
Kolomitsyn, I. V.; Kildyshova, L.; Green, D. A. “Weak Anion Exchange Particulate Medium Prepared from Phenol-Containing Organic Matter from Anions Contained in Aqueous Solutions” US Patent **10,722,878B1** Jul 28, **2020**.

Kolomitsyn, I. V.; Jones, P.W.; Green, D. A. “Particulate Sorption Medium Prepared From Partially Decomposed Organic Matter For Selective Sorption Between Competing Metal Ions In Aqueous Solutions” US Patent **10,173,213**, January 08, **2019**.

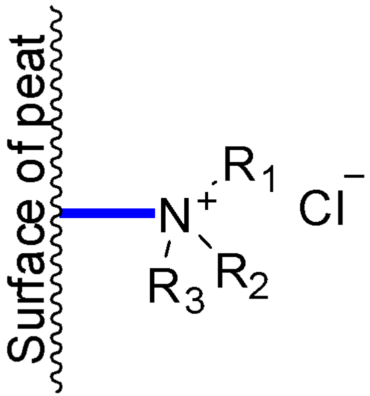
Kolomitsyn, I. V.; Jones, P.W.; Green, D. A. “Particulate Sorption Medium Prepared from Partially Decomposed Organic Matter” US Patent **9,561,489**, February 7, **2017**.

Peat Derived Anion Exchange Resins to Remove Sulfate

Weak base

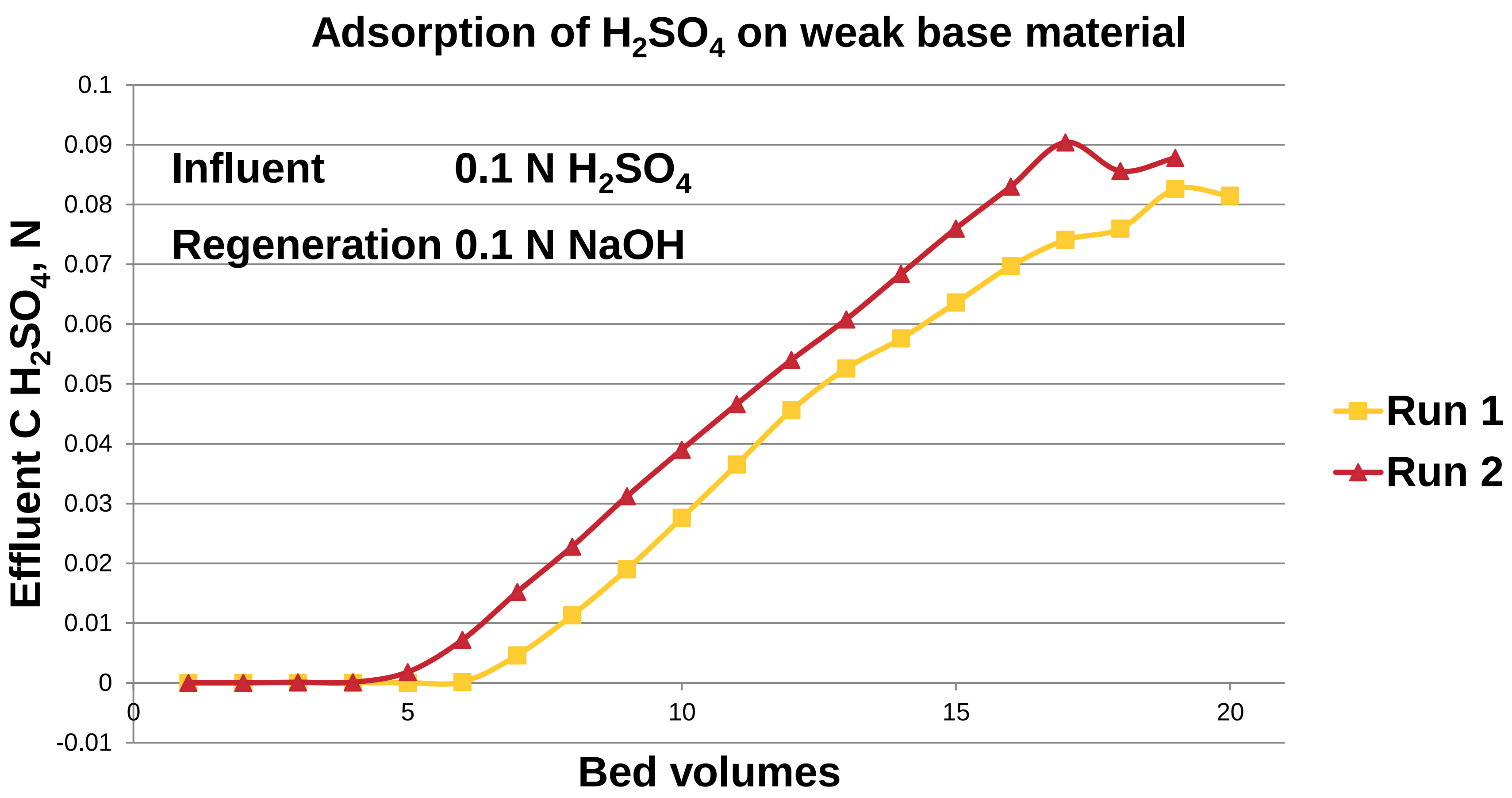


Strong base



Goal	Achieved
• Granules (hardness)	
• Stability (up to pH=12.0, t = 100^{o}C)	• Stable at pH = 1.0 - 12.0
• Capacity: 350-400 mEq/100 g	• 360 mEq/100 g
• H_2SO_4 process activity/capacity	• Demonstrated at pH = 1.0 – 8.0
• Operation cost vs anion exchanger	
• Natural weak base and strong base	• Achieved

Peat derived weak base anion exchange material

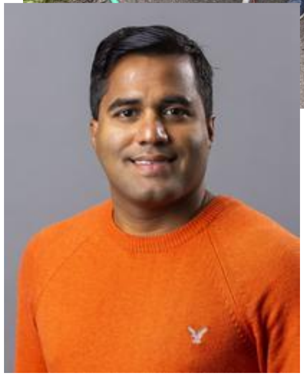


Peat Based Anion Exchange Material: Status

- Patented material and process
- Active across a wide range of pH conditions
- Material can be regenerated
- Laboratory testing is complete
- Likely to be cost-effective compared to existing anion exchange materials
- Has yet to be pilot-tested under field conditions.

Chemical Precipitation Team

Mr. Shashi Rao



Mr. Shashi Rao

Dr. George Hudak

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Team:

Dr. Meijun Cai

Mr. Shashi Rao

Ms. Sara Post

Mr. Matt Anthony

Dr. George Hudak

Dr. Lucinda Johnson

Dr. Adrian Hanson*

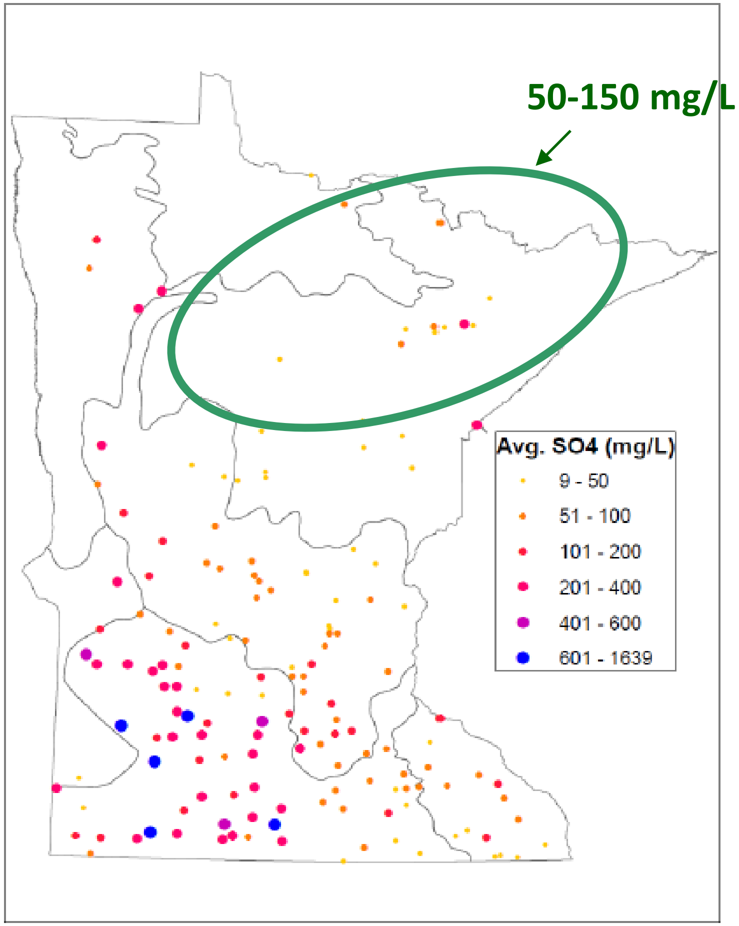
Funding

- LCCMR
- NRRI PUFT

* Collaborator (retired UMD)

Chemical Precipitation Treatment

Average Sulfate Concentration of Municipal WWTPs

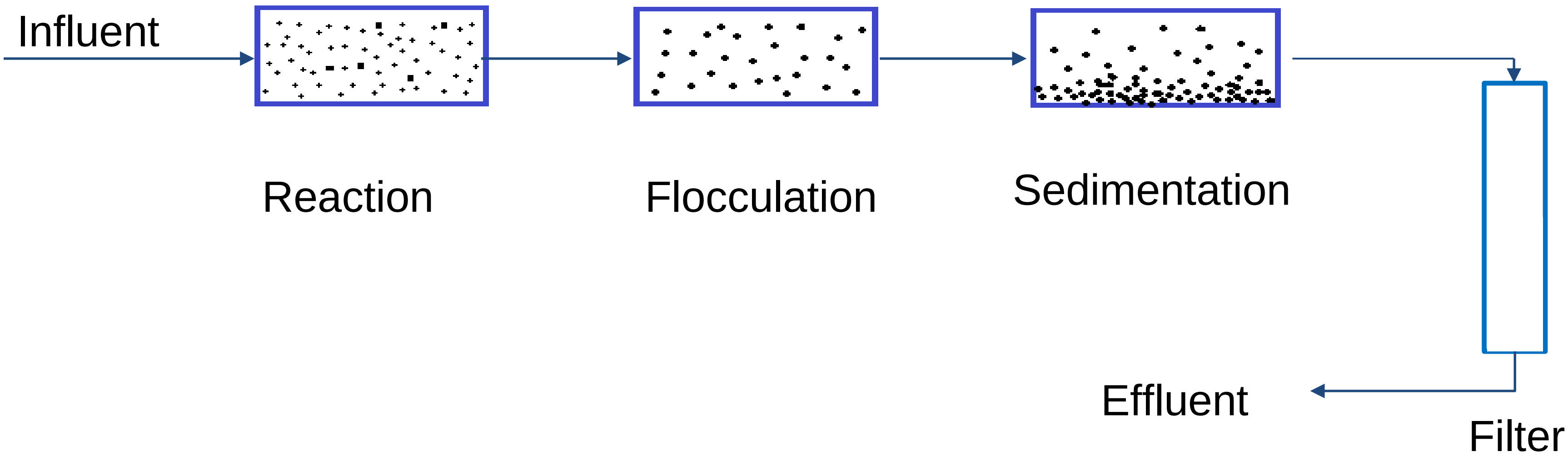


GOALS

- Evaluated barium precipitation and solid-liquid separation methods for treating municipal wastewater to reduce sulfate concentration below 10 mg/L.
- Provide a framework for decision-making when considering barium precipitation sulfate removal technology.

Chemical Precipitation Technology

- To evaluate if the chemical precipitation technology can reduce sulfate from 50-350 ppm to below 10 ppm or other desired levels.
- Process: 1.Use $BaCl_2$ to react with SO_4; 2. clump fine precipitate to flocs; 3. sediment and filter to remove barium sulfate particles



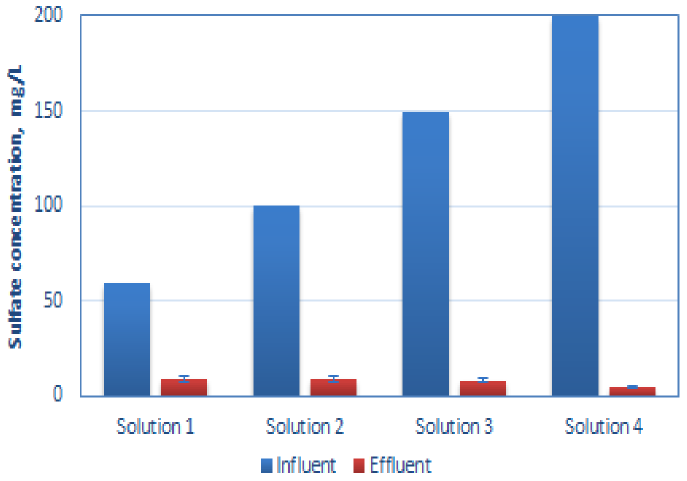
Laboratory Chemical Precipitation Tests

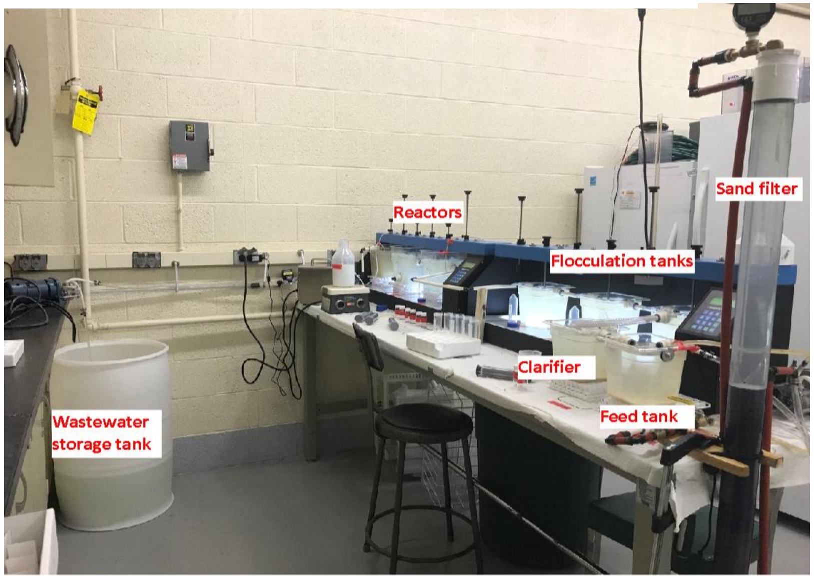
Municipal wastewater tested

- Aurora: 200-300 mg/L
- Grand Rapids: 80-120 mg/L
  with chelating organics
- Virginia: 60 mg/L
- WLSSD: 200-400 mg/L

Other water tested

- City of Aurora tap water, 300-400 mg/L
- St. James Pit Lake water, 300-400 mg/L





Batch testing at NRRI

Field Pilot Trial in 2021

Plant A

Domestic wastewater only

Sulfate level: ~60 ppm

Test flow rate: 2 gallon/minute

Trial duration: June 4th – August 2nd

Plant B

Domestic + Industrial wastewater

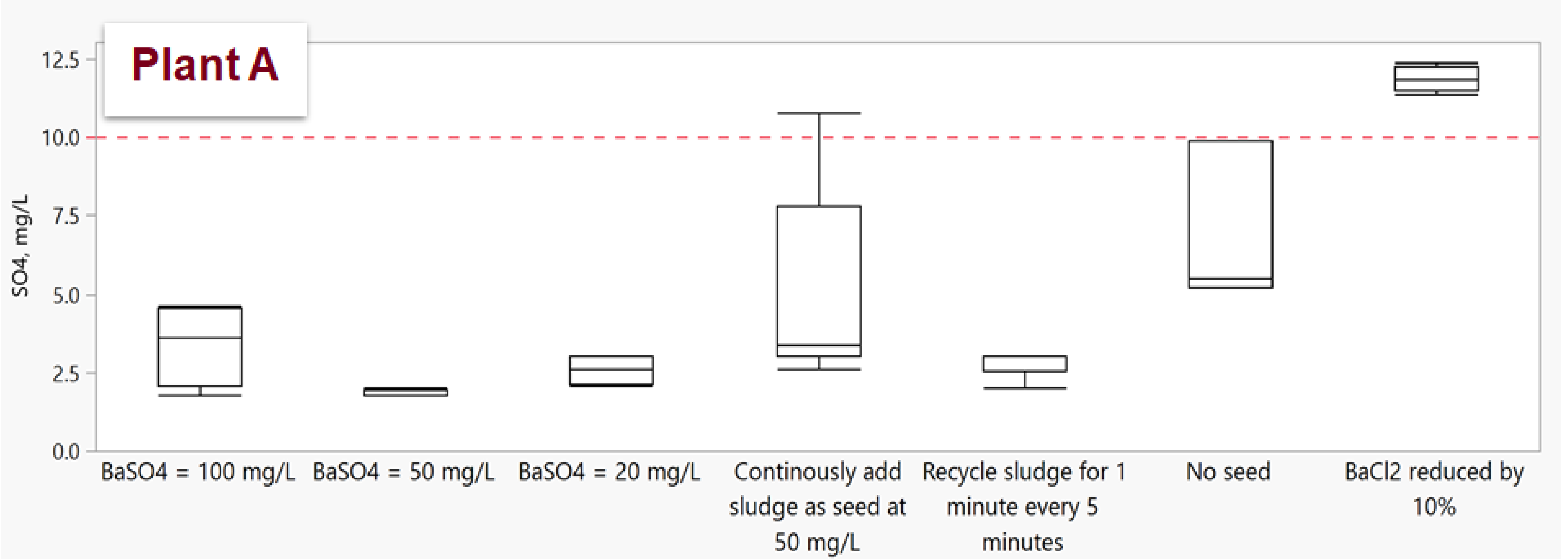
(contain chelating organics)

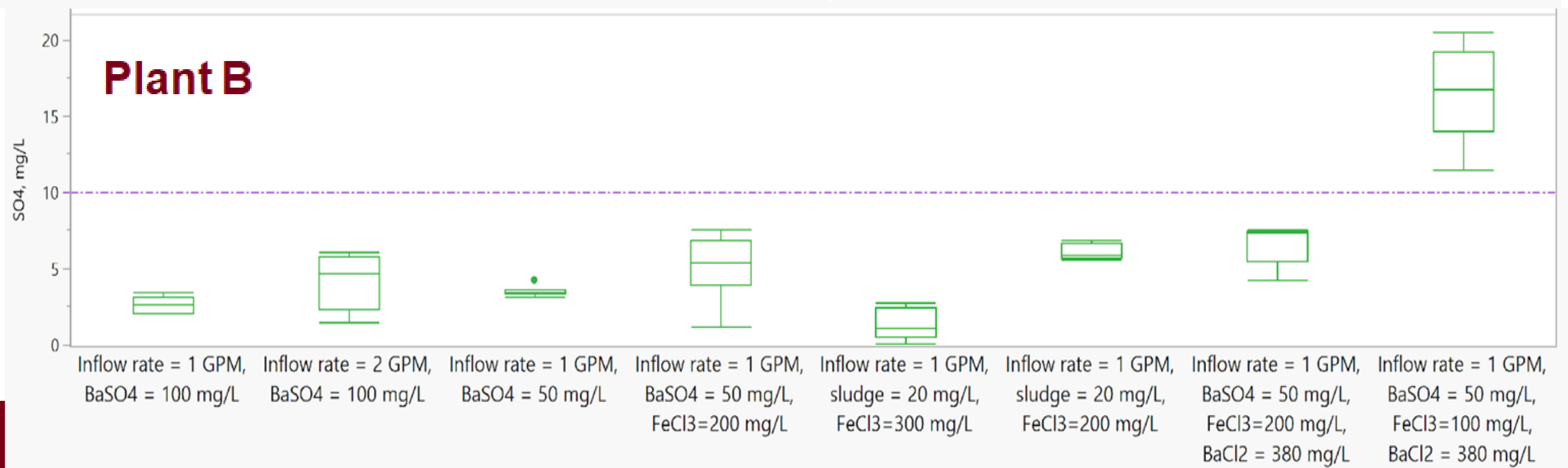
Sulfate level: 85-115 ppm

Test flow rate: 1 gallon/minute

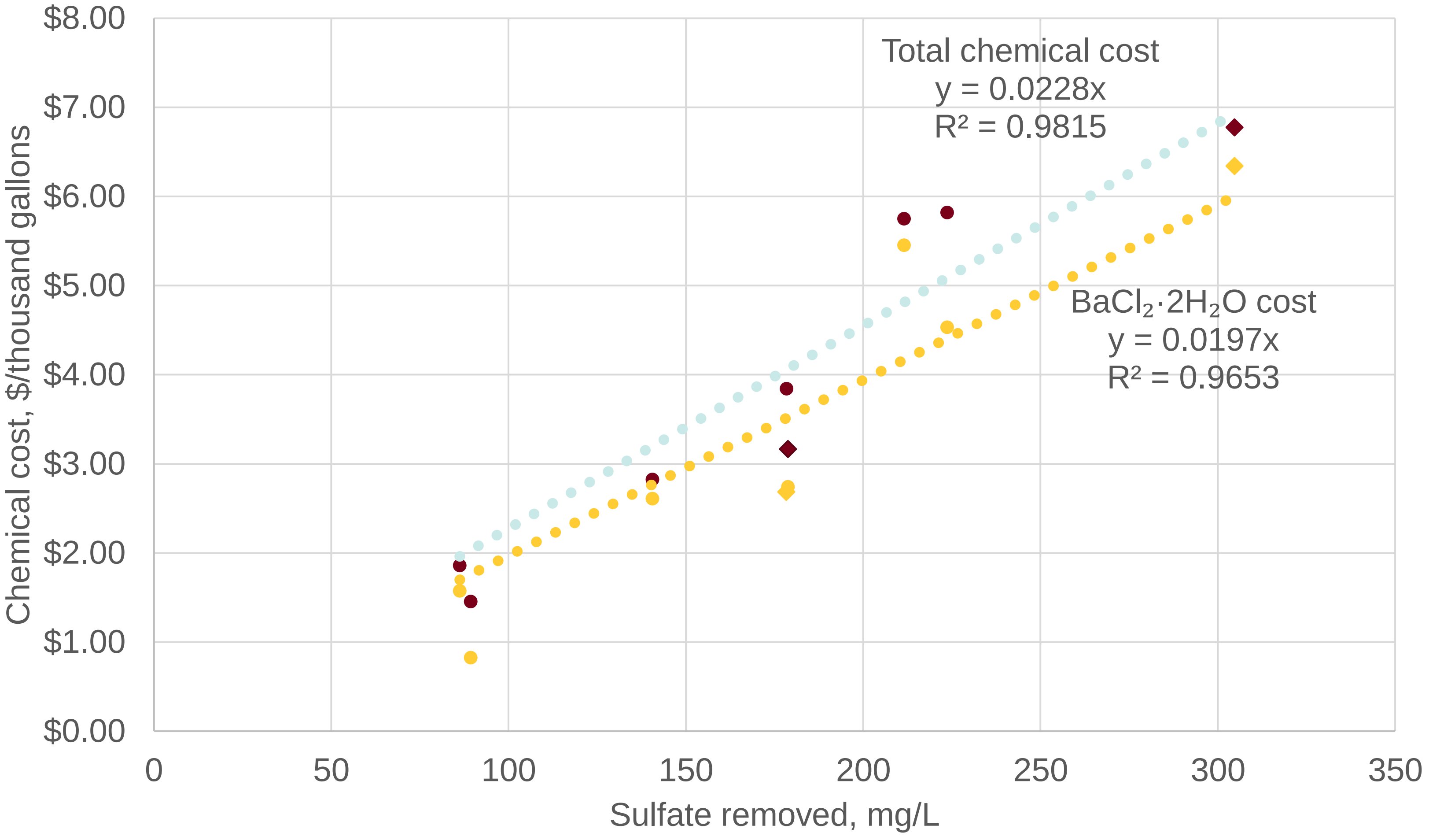
Trial duration: August 26th – October 8th

SO_4 Concentrations in Effluent





Pilot Test Results – Chemical Cost



Summary

- Chemical precipitation with barium chloride effectively reduces sulfate concentrations to below 10 mg/L.
- Should be considered a “polishing” treatment, especially with high-mass influent.
- Influent water quality (e.g., presence of chelating organics) influences test conditions, but can be managed at pilot scales.
- Cost of chemicals is a linear function of influent sulfate concentrations.

Biological Treatment Team:

Biological Sulfate Reduction Coupled with Iron-Based Sulfide Immobilization

Chan Lan Chun

Nathan Johnson

R. Lee Penn

Yawkey Minerals Management LLC

minnesota power

MnDRIVE
Advancing Industry, Conserving our Environment

Natural Resources Research Institute
University of Minnesota Duluth
Driven to Discover

UMD
SWENSON COLLEGE OF SCIENCE & ENGINEERING
University of Minnesota Duluth
Driven to Discover

CHEMISTRY

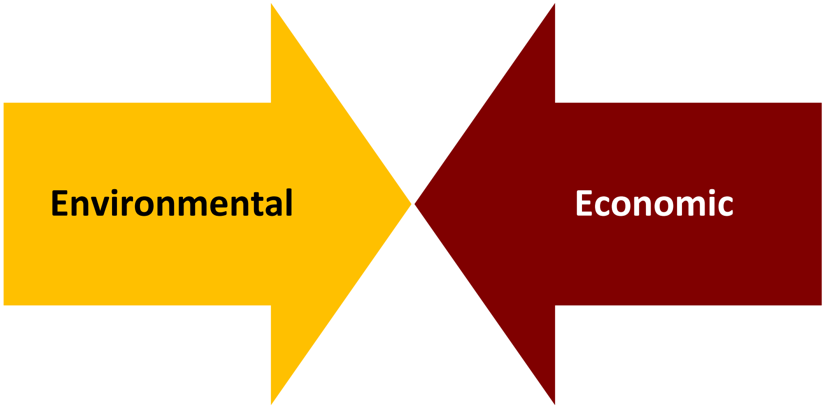
DEPARTMENT OF HEALTH

Funding: MnDRIVE

Biological Sulfate Treatment

Lower-cost and more flexible treatment than membrane-based technologies

- *Less sulfate to environment*
- *Benefits for wild rice, drinking water*



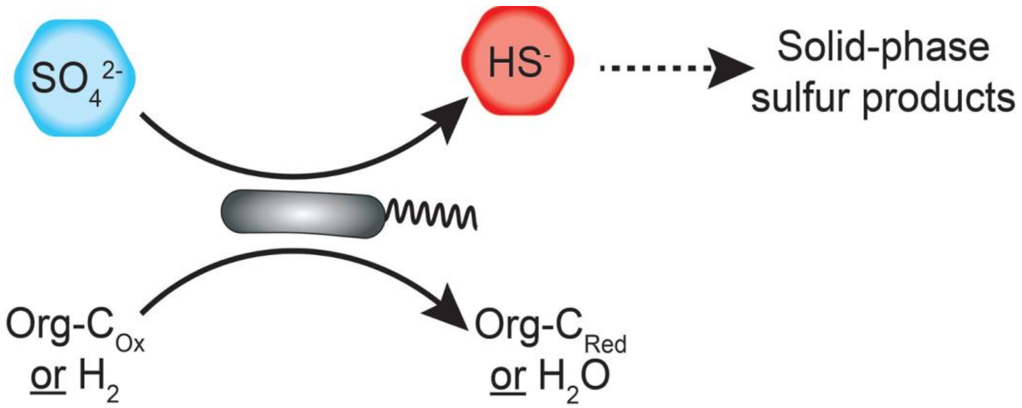
- *Limit scaling*
- *Can support reuse*
- *Lower costs than membrane treatment*

Challenges of Biological Sulfate Treatment

- Biological sulfate reduction is commonly applied for metal and sulfate remediation.

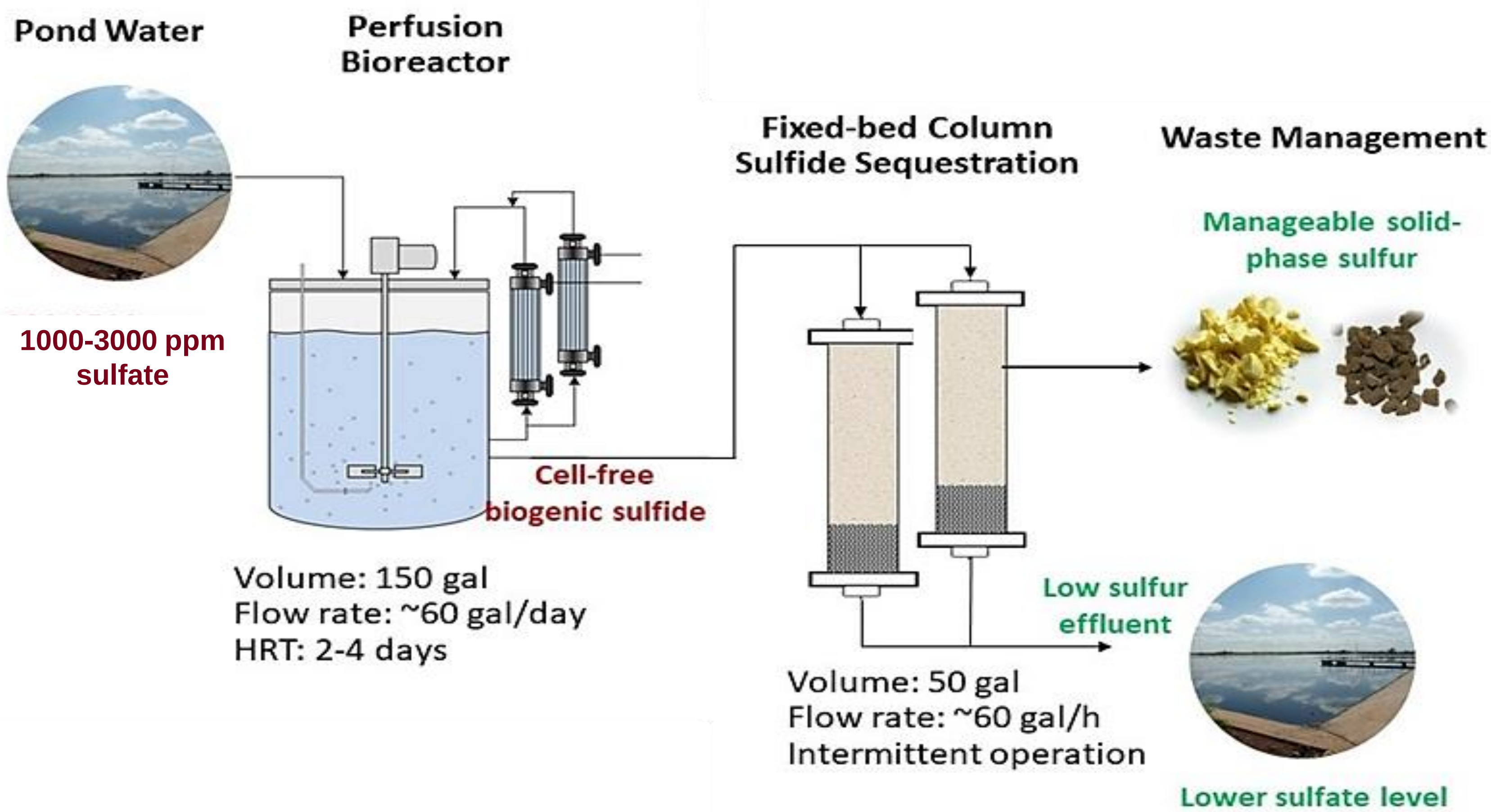
- Biokinetics of sulfate reduction is **slow** as an anaerobic metabolic process.

- Sulfate reducing bacteria mediate the conversion of **sulfate** to **sulfide**, which can be recovered as inert, non-toxic solid sulfur species.



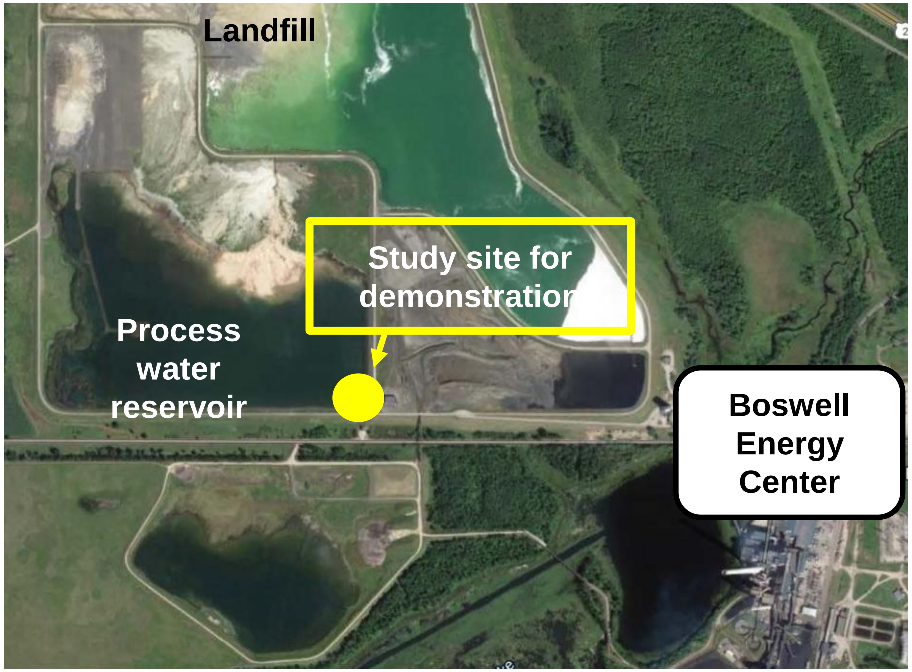
Two-Stage Sulfate Treatment System

Goal: Demonstrate biological sulfate treatment with iron – based immobilization to remove sulfate in high-strength wastewaters



Field demonstration of the treatment system

Sulfate-rich industrial process water: Flue Gas Desulfurization (FGD) Process Water



1) verify the rates of biological and iron-sulfide reactions and byproduct composition,
2) evaluate hydraulics and flow rate in relation to biofilm fouling, filtration particle size, and backwashing for system operation, and
3) evaluate implications of co-occurring water chemistry and site-specific problems for reliability of potential full-scale treatment development

Treatment system

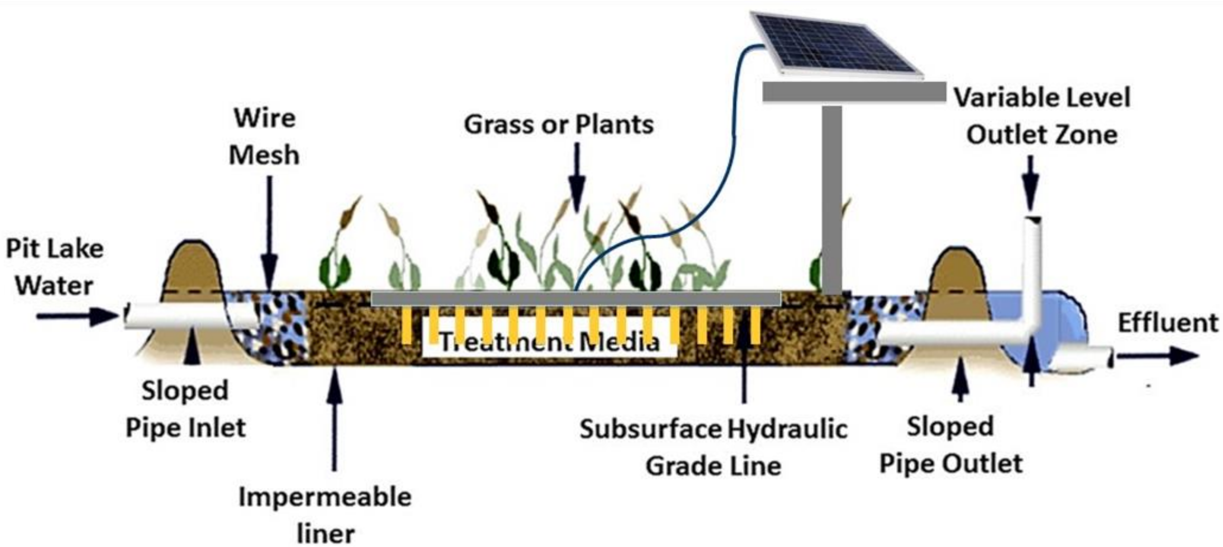
Research Summary and Outlook

- Targeted, ion-specific sulfate removal treatment
- Pilot-scale biological sulfate treatment with low flow (rate: 20-30 g S/day; capacity: 5-20 mg S/$g_{solid\ phase}$ at~0.02 GPM)
  - ➡ Scalable to an industrial-relevant scale system
- Manageable solid sulfur products
  - ➡ Easier and cheaper waste management
- Stability of post-reaction materials
  - ➡ Solid management conductions and realistic storage time

In Situ Electrode-Integrated Sulfur Remediation

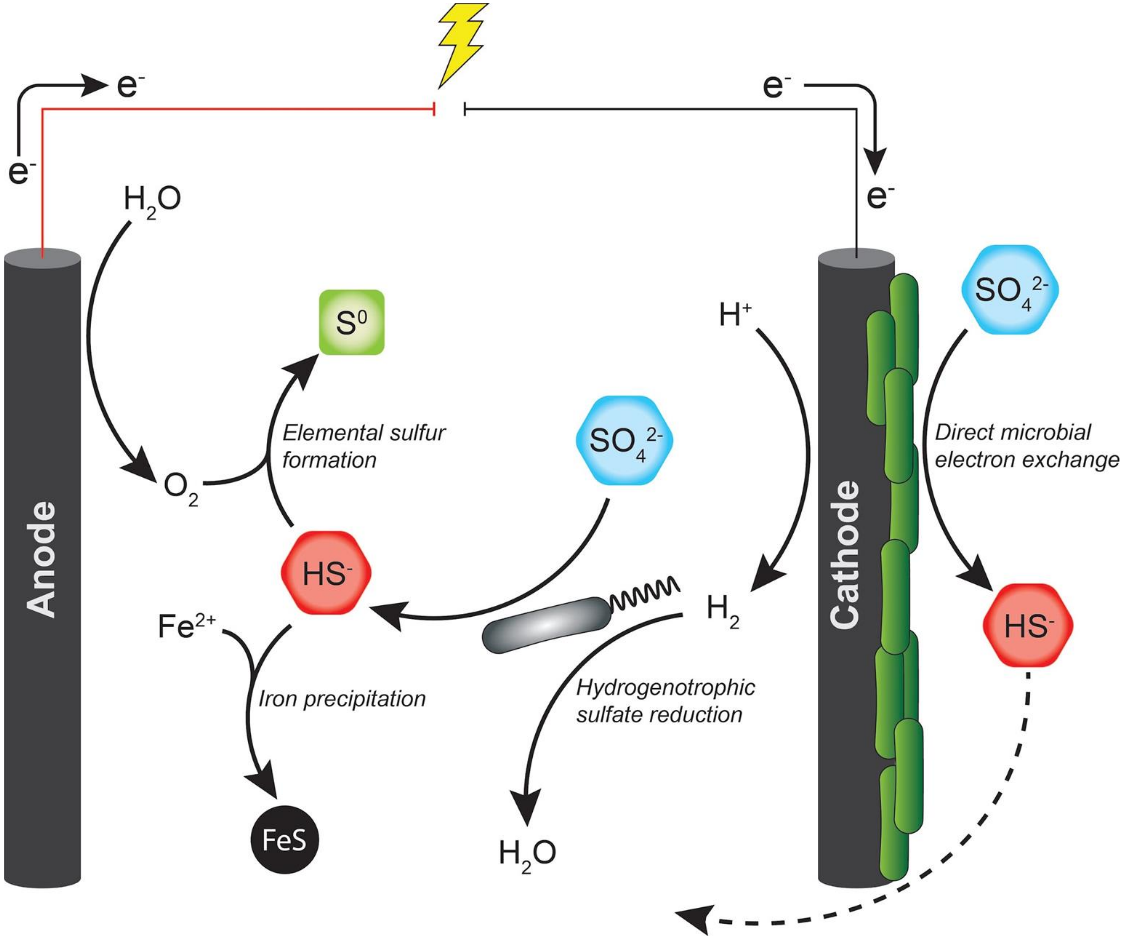
Chan Lan Chun and Matthew Berens
University of Minnesota Duluth

Randy Kolka
USDA-FS Northern Research Station



Funding: USDA FS

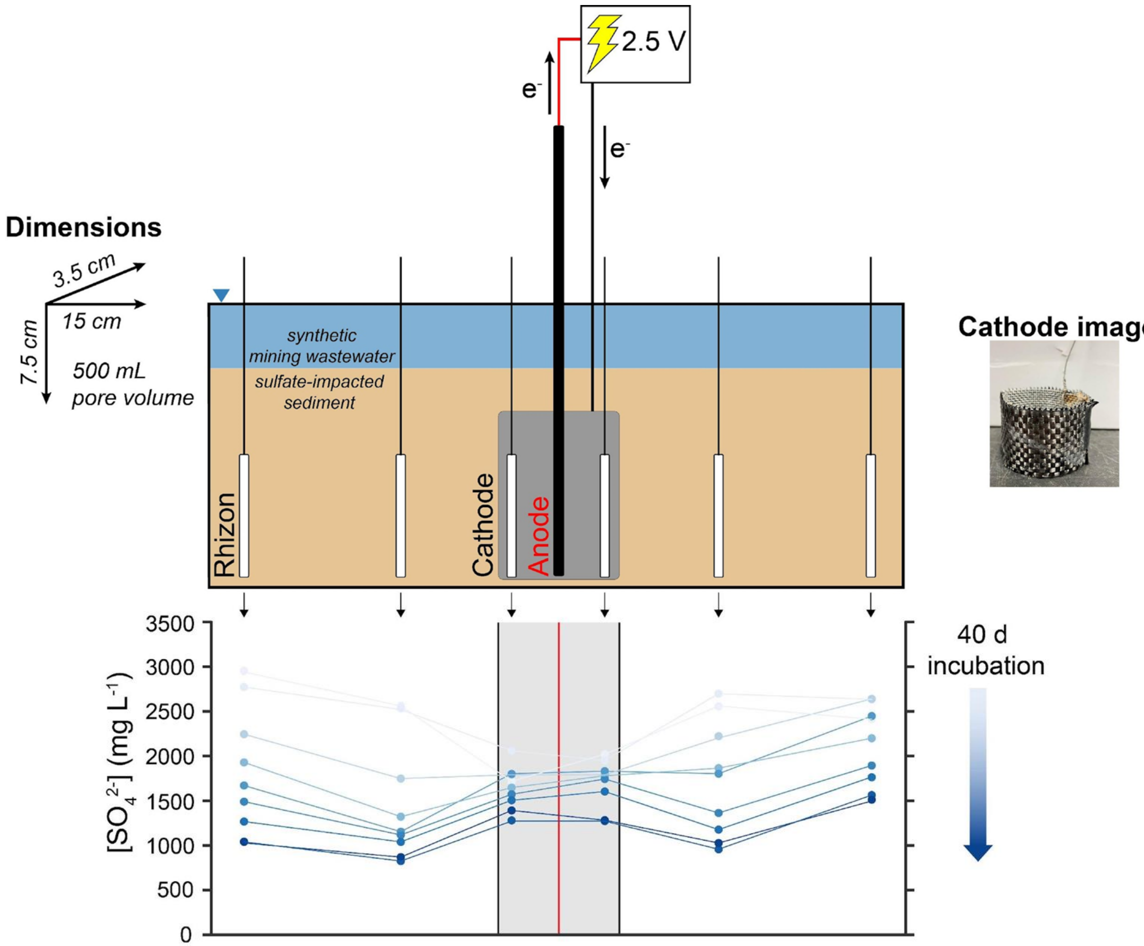
Electrochemical Bioremediation



- H_2 production at the cathode
- Microbial SO_4^{2-} reduction
- Removal as FeS_x
- Recovery as S^0
- Potential for direct e^- exchange

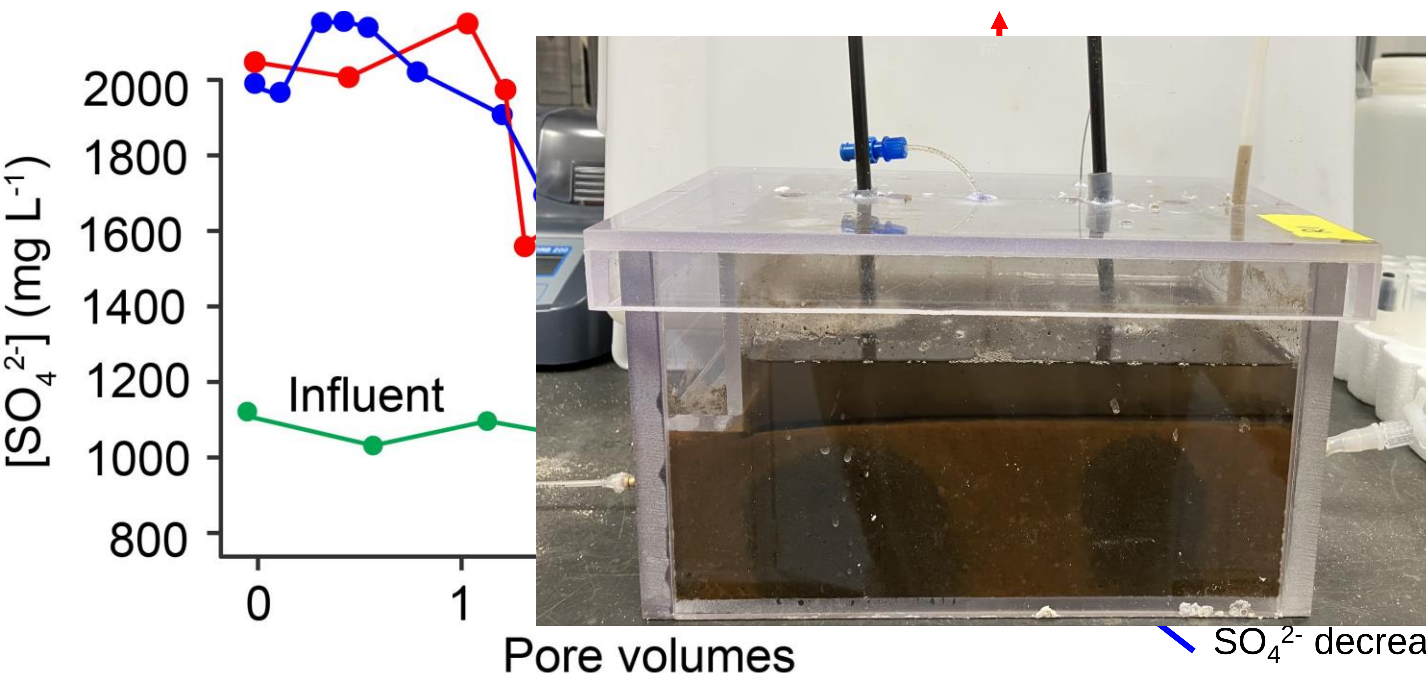
Batch Experiments

- SO_4^{2-}- and Fe-impacted sediment
- Synthetic mining runoff (1000 ppm SO_4^{2-})
- SO_4^{2-} decreased up to 2000 ppm
- Higher SO_4^{2-} reduction near cathode where H_2 is produced



Unpublished Data

Lab-Scale Flow-Through Demonstration



m native

SO_4^{2-} decreased up to 1000 ppm over 4 pore volumes

Unpublished Data

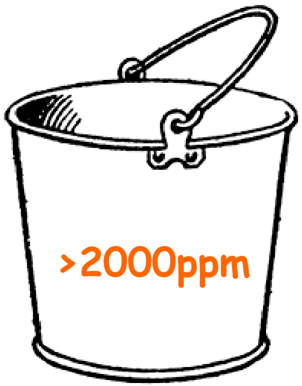
Research Summary and Outlook

- Continue flow-through experiments to determine maximum potential sulfate removal.
- Determine relationship between sulfate reduction and applied voltage at different sulfate loadings and flow rates.
- Ongoing collaborations to study the stability of FeS under different environmental conditions.
- Plan for potential pilot- and demonstration-scale testing as an in-situ treatment option.
- Long term: Apply technology to other pollutants with similar redox cycles, such as selenium

Sulfate Treatment: Three Regimes

Municipal water treatment facilities

Agriculture, Industry, Mining Pit Lakes



Power Generation Effluent Treatment

Technology Solutions:	Chemical Precipitation	Biological Reactors; Anion Exchange?	Biological Reactors; Anion Exchange?

Each individual challenge may require portfolio of two or more technologies applied in combination

Closing Thoughts

Meeting Minnesota's restrictive sulfate standard for wild rice waters is a challenge.

Multiple solutions will be required to address high-mass removal in neutral, low-metal applications.

Chemical precipitation appears to be a viable alternative to membrane technology for applications in the range of 250 mg/L and below.

High-mass removal will likely involve multiple technologies, including biological treatment systems.

- Permanent University Trust Fund
- MN Legislature & LCCMR
- Mn Department of Health
- MN Power
- US Forest Service
- Mn DRIVE
- Yawkey Minerals Management LLC
- Municipal wastewater treatment plants
- APT, Inc.
- Process Research Ortech Inc.
- NRRI & UMD PostDocs, technicians, UMD graduate and undergraduate students
- NRRI Coleraine Engineering staff

Natural Resources Research Institute

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Research Support Manager 3: Water Research Leader

Job ID: 351760
Location: Duluth
Employee Class: Acad Prof and Admin

https://nrri.umn.edu/about/employment-opportunities