Energy-efficient selective removal of metal ions from mining influenced waters (MIW) using H-bonded Organic-Inorganic Frameworks (HOIFs)

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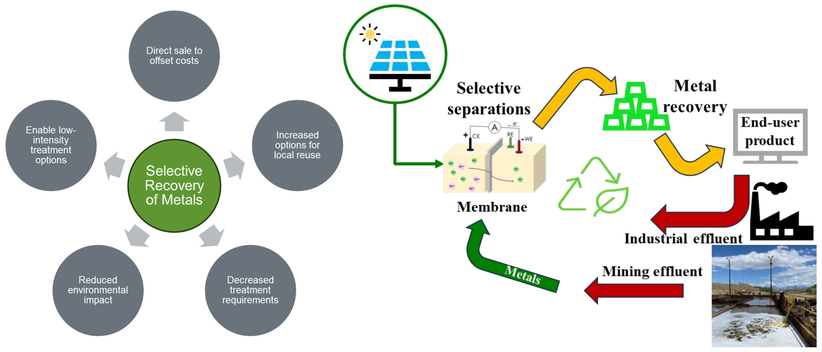
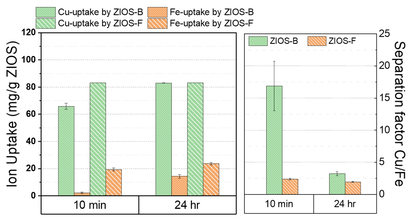
Mining Influenced Water (MIW) is a widespread domestic & international environmental challenge



Mine wastes exposed to air, water and bacterial activity can generate significant amounts of MIW, including acid and metalliferous drainage (AMD). As AMD is generated, it leaches metals from surrounding rocks. There are 20k-50k sites across the US producing MIW leading to the pollution of over 10,000 km of waterways and incurring significant costs for authorities and mining operations.

A novel alternative for efficient and selective metal recovery from MIW by HOIFs

HOIFs are adsorbents with fast kinetics, high specificity and capacity under acidic conditions



HOIFs (Batch ZIOS-ZIOS-B and Flow ZIOS-ZIOS-F powder in this case) have demonstrated impressive potential for Cu^{2+} recovery in lab trials under AMD relevant conditions – both in terms of rate and specificity.

Project Objectives

- *Develop HOIF based mixed matrix membrane*
- *Demonstrate viable metal capture/recovery with HOIF mixed matrix membrane*
- *Mechanism of Cu^{2+} uptake understood*
- *Techno-economic feasibility demonstrated*

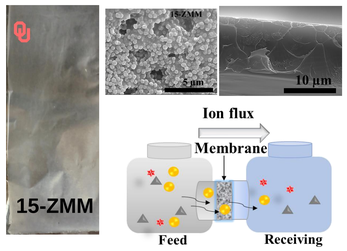
Levelized cost of copper recovery using current technologies is not attractive

Technology	Copper recovery from AMD	Levelized cost of copper recovery (LCM)	Levelized cost of water treatment (LCW)	Notes
Copper scavenger cells using scrap iron and requiring smelting	80% recovered 85% purity	$1.53/kg-Cu	$0.57/m³	- Cost of smelting and extra slag production included (2022 figures)
Amine based resins that can operate at low pH and highly selective for copper	90% recovered 98% purity	$43/kg-Cu	$18.05/m³	- Assume recovered brine is processed in existing electro-winning process - Resin has capacity of 50mg-Cu/g and has been demonstrated to be reused 50 times in lab control studies
ZIOS	**95% recovered 98% purity**	**- $4.14/kg-Cu (income generation)**	**- $1.83/m³ (no cost water treatment)**	- Assume ZIOS is processed in existing electro-winning process - ZIOS has capacity of 120mg-Cu/g and assumed to be reused 50 times

AMD at pH 2.6 with flow of 600 gpm (136 m³/h) with copper concentration of 3.88 lb/1000 gallons (465 mg/L)

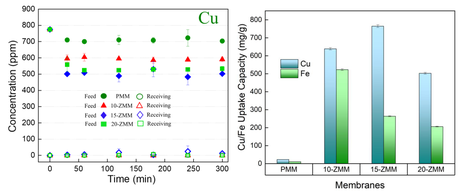
Key Results

ZIOS mixed matrix membrane (ZMM) successfully fabricated and demonstrates ion selectivity in AMD



ZIOS membrane and SEM images of 15-ZMM (ZMM with 15% w/w ZIOS integrated).

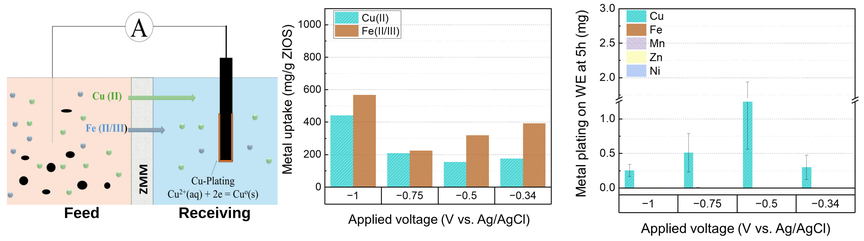
Diffusion set-up integrating a ZMM for sequential adsorption of Cu and migration of non-target metals over time.



High Cu selectivity behavior of ZMMs after 5 h of exposure in real AMD in diffusion cell. Uptake of Cu and Fe occurs very quickly, with significantly more Cu removal demonstrated by the ZMM membranes compared to pristine PES membrane (PMM)

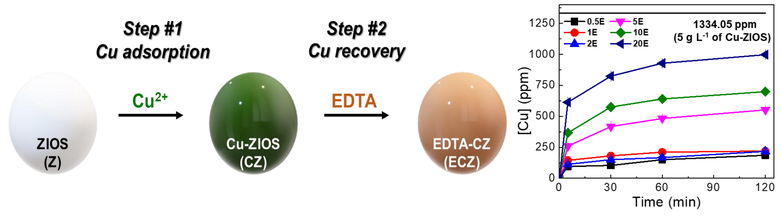
Real AMD waters (2 sources) from a Rio Tinto site and have pH of 2.3-2.6. Complexity of real AMD does not reduce ZIOS' membrane ability to remove copper from AMD and retain a degree of selectivity for copper.

AMD Electrodialysis with ZMM recovered copper metal



Electrodialysis tests with ZMM using AMD indicate that Cu metal can be selectively recovered by electroplating on a working electrode (WE). Major contaminant is iron. Copper is found in the ZMM and on the WE, with the proportion of Cu recovered on the WE influenced by the applied potential. Demonstrates potential for efficient, selective recovery of Cu metal directly from AMD in a scalable process.

Copper recovery from ZIOS powder by EDTA treatment



Initial results indicate that Cu metal can be recovered directly from Cu-adsorbed ZIOS (CZ) by a simple EDTA treatment. This has significant potential as an efficient and effective pathway for valorization of Cu from MIW. This approach to Cu recovery adds another potential option for operators to recover Cu from MIW.

ZIOS has demonstrated that it can selectively recover copper directly from AMD and is potentially competitive with current best available technology

NAWI CONNECTIONS

Period of Performance: 12/14/2022 – 12/31/2025

Challenge Area/Topic Area: Precision Separations Topic Area
Project aims to radically improve process selectivity (water treatment performance), energy efficiency (energy performance) while reducing energy-related emissions (human health and environmental externalities) in the treatment of wastewater from mines

NAWI Leverage
The project will be leveraging National Lab resources made available through NAWI. The project will also rely upon NAWI TAP3 to review and assess technology viability

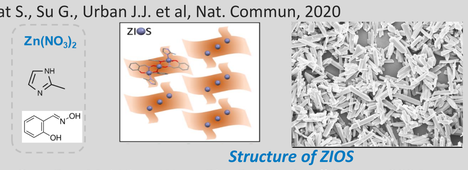
KEY FINDINGS AND CONCLUSIONS

- ✓ **Successful fabrication of ZIOS membranes**
- ✓ **Confirmed the structural stability of ZIOS mixed matrix membranes in real AMD**
- ✓ **Confirmed the copper uptake capacity of 765 mg/g for 15-ZMM by diffusion test and selectivity behavior in real AMD**
- ✓ **Confirmed that copper can be recovered from ZIOS through EDTA treatment with 75% efficiency**
- ✓ **Preliminary costing indicates ZIOS can be produced <$20/kg with production at ambient conditions**
- ✓ **Levelized cost of copper recovery and water treatment significantly better than current alternative technologies**

REFERENCES

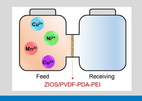
Bui N., Kang H.M., Teat S., Su G., Urban J.J. et al, Nat. Commun, 2020

Zinc Imidazole Salicylaldoxime supramolecule (ZIOS)



Structure of ZIOS

T. C.. Le Van, P. Nguyen Quy, Duy Mai Hien, Wang Bin, Bui N., Small Struct., 2024



	Cu^{2+}	Ni^{2+}	Co^{2+}	Mn^{2+}
Ionic radius (Å)	0.73	0.69	0.75	0.83
Hydrated radius (Å)	2.97	3.02	2.95	2.86

ACKNOWLEDGEMENTS

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