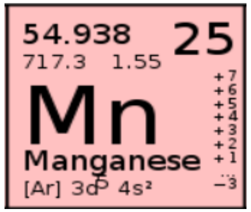

Electrolytic **manganese removal** from acid rock drainage

Sarah Doyle[1], Linda Figueroa[2]

1: Itasca Denver Inc.; 2: Colorado School of Mines

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WVTF IMWA 2024

Mine Drainage in Colorado

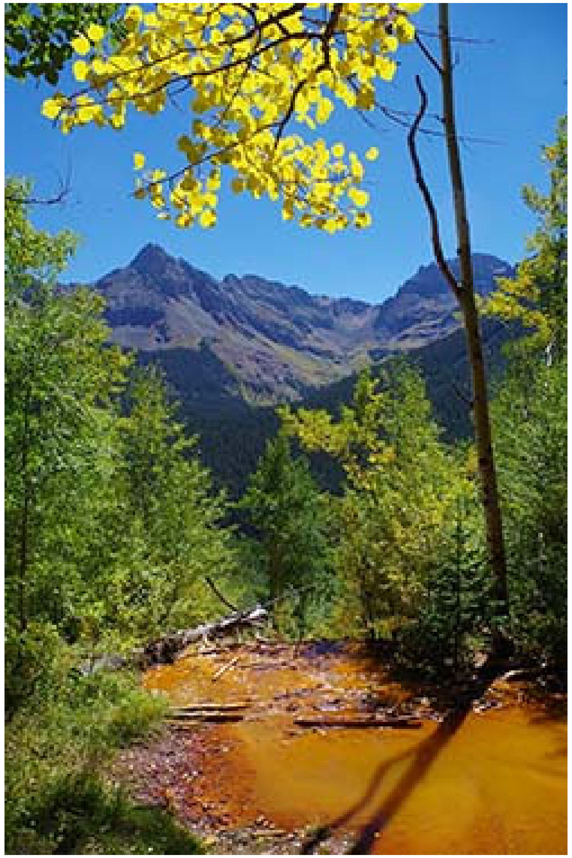
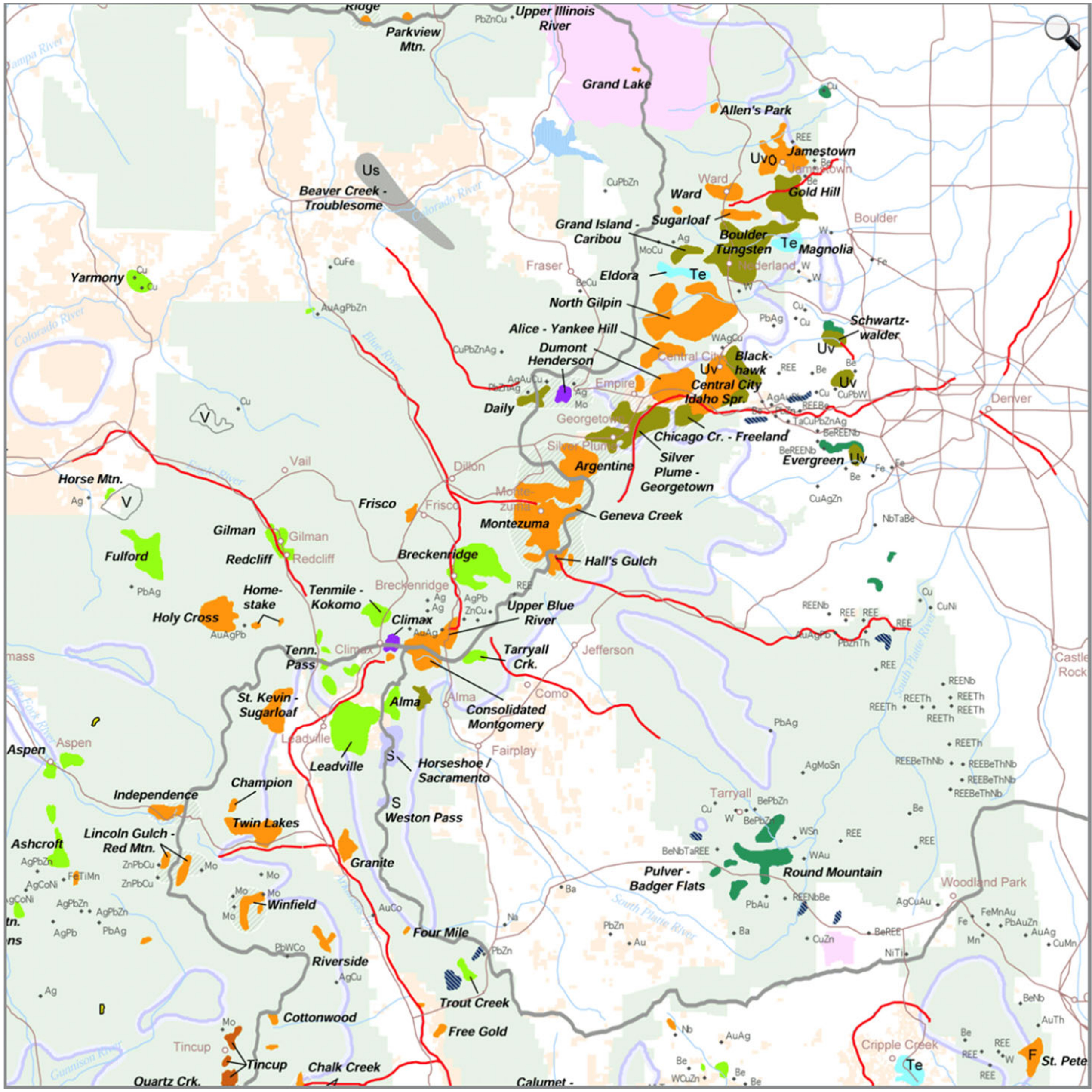


Photo: CDPHE & DNR, Colorado Abandoned Mines Water Quality Study Data Report - June 2017 https://www.colorado.gov/pacific/cdphe/wq-mining

Historic mine wastes near Leadville, Photo: Sarah Doyle

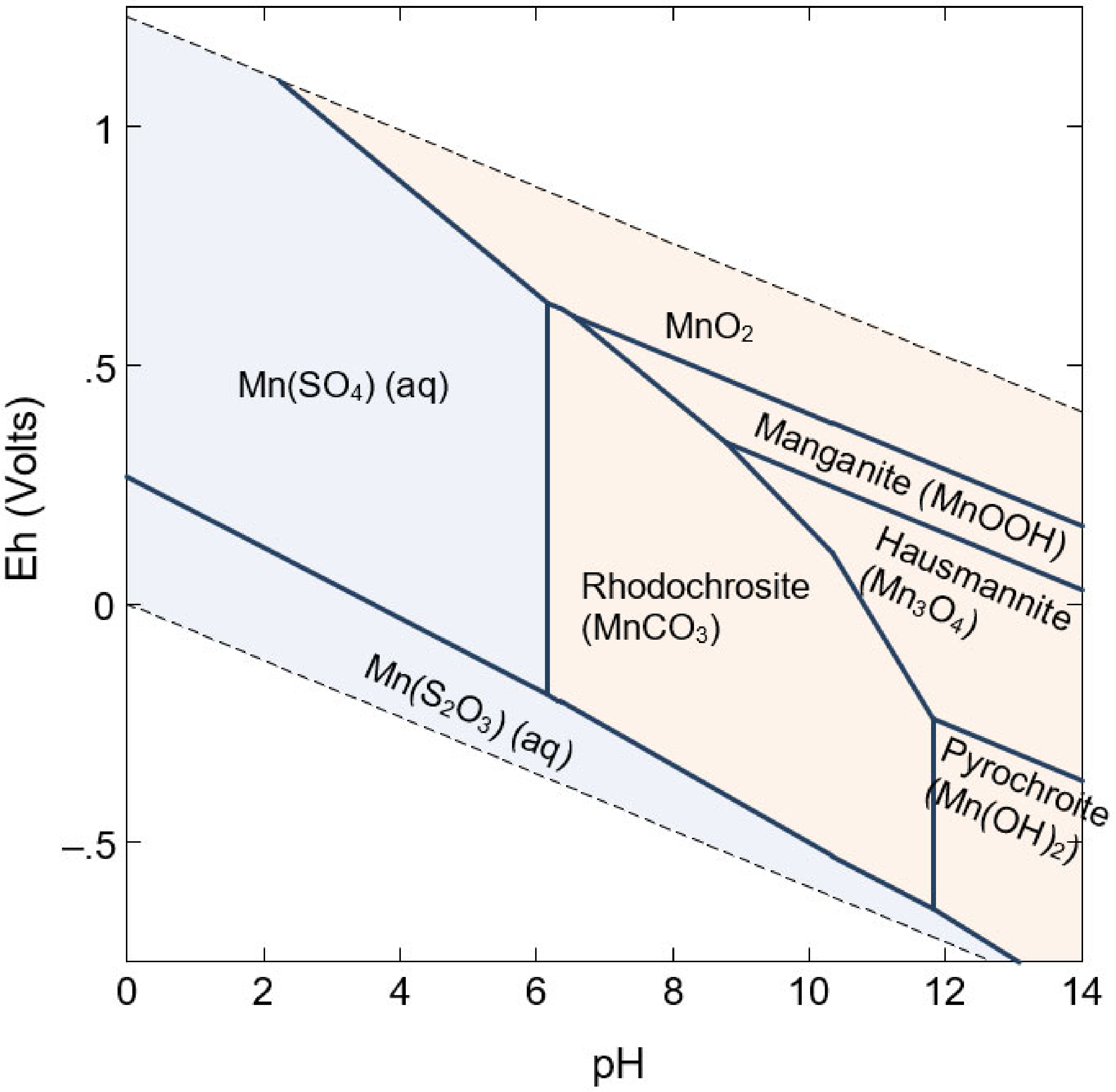
Potential Metal-Mine Drainage Hazards in Colorado



Map prepared by Colorado Geological Survey

Manganese Occurrence

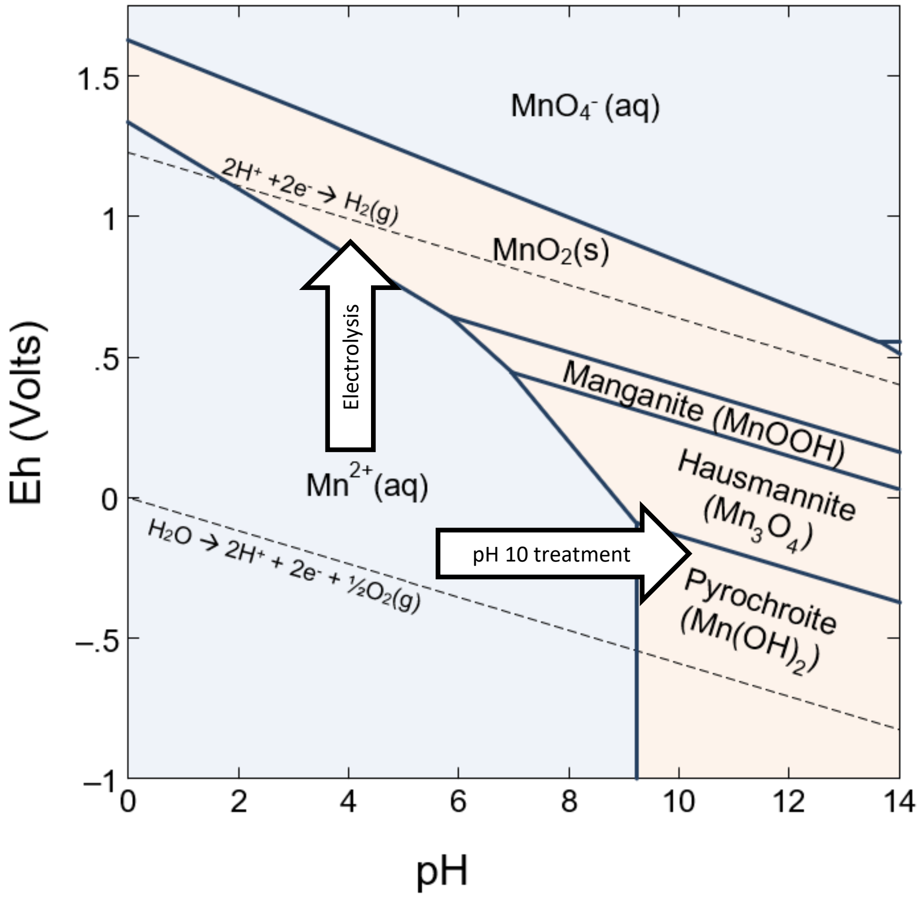
- Manganese oxides are common mineral phases
  - Well known scavengers of metals
  - Chemically active – redox and pH sensitive
- In mine drainage, acidic conditions mobilize Mn
  - Typically <50mg/L
  - up to 259 mg/L at Gilson Gulch in Idaho Springs (Holm and Crouse 2009)



Mn Removal from ARD

Mn removal at high pH occurs over wide Eh range

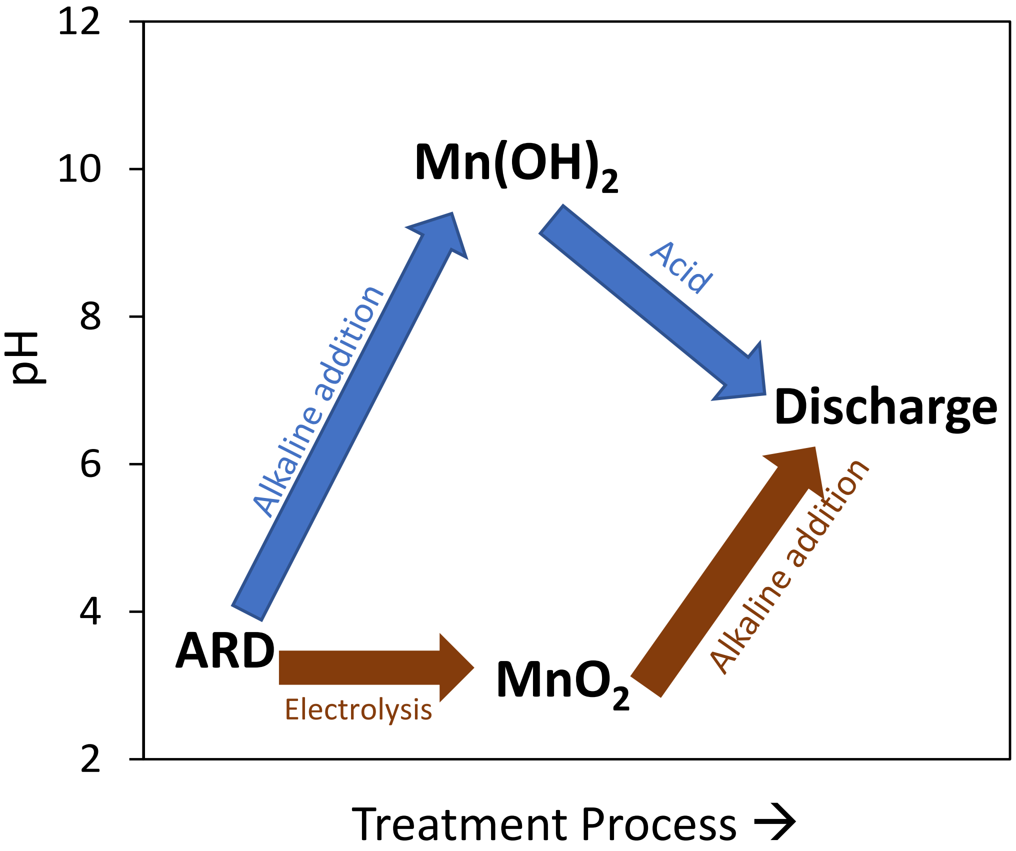
Mn removal at low pH requires high Eh



Electrochemical Advantages over Alkaline Treatment

Electrochemical Treatment Advantages

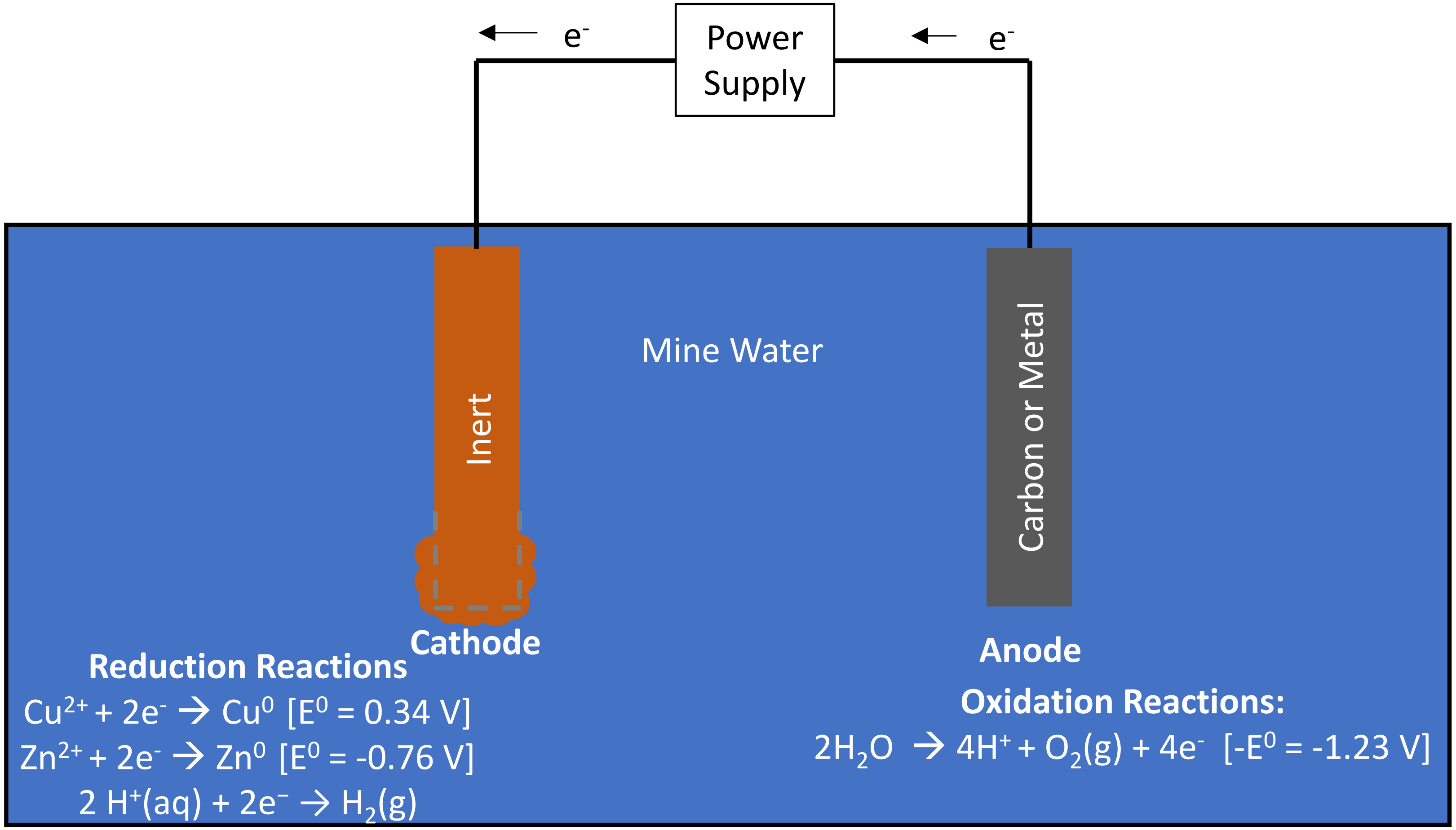
- Reduced chemical costs
- Elemental and condensed metal forms
- Potential for recoverable product
- Voltage requirement is low



Alkaline Treatment Disadvantages

- Chemical costs
- Difficult to dewater sludge
- Metals not easily recovered
- Sludge requires disposal

Electrolysis cell (system used)



← e^-

Power Supply

← e^-

Mine Water

Inert

Carbon or Metal

Cathode

Reduction Reactions

$Cu^{2+} + 2e^- \rightarrow Cu^0$ [$E^0 = 0.34$ V]

$Zn^{2+} + 2e^- \rightarrow Zn^0$ [$E^0 = -0.76$ V]

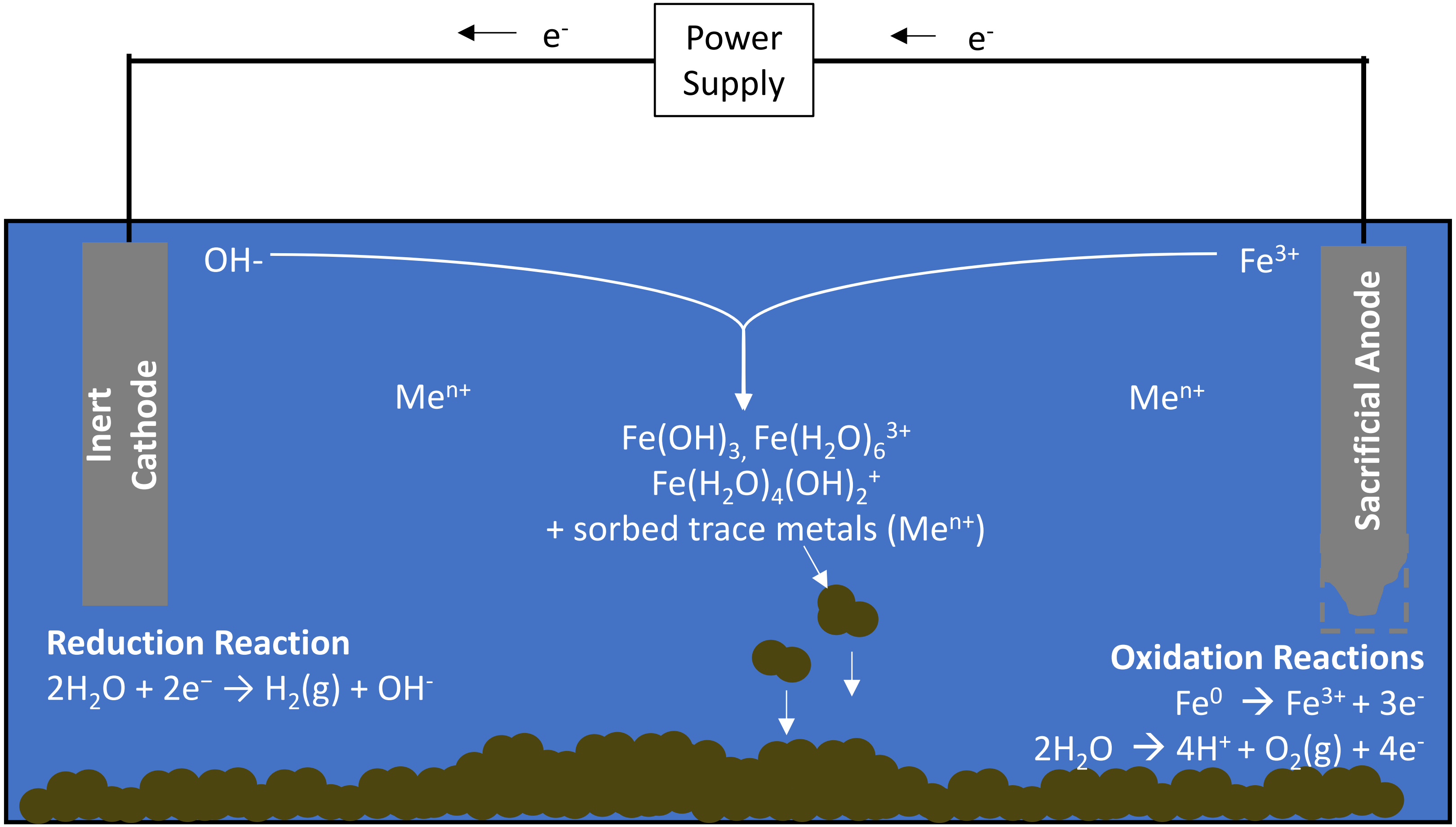
$2\ H^+(aq) + 2e^- \rightarrow H_2(g)$

Anode

Oxidation Reactions:

$2H_2O \rightarrow 4H^+ + O_2(g) + 4e^-$ [$-E^0 = -1.23$ V]

Electrocoagulation (not the system used)



$\leftarrow e^-$ Power Supply $\leftarrow e^-$

Inert Cathode

Sacrificial Anode

OH^-

Fe^{3+}

Me^{n+}

Me^{n+}

$Fe(OH)_3$, $Fe(H_2O)_6^{3+}$

$Fe(H_2O)_4(OH)_2^+$

+ sorbed trace metals (Me^{n+})

Reduction Reaction

$2H_2O + 2e^- \rightarrow H_2(g) + OH^-$

Oxidation Reactions

$Fe^0 \rightarrow Fe^{3+} + 3e^-$

$2H_2O \rightarrow 4H^+ + O_2(g) + 4e^-$

Goal: Improve Electrolytic Metal Removal from ARD

Previous Electrolytic Mn Removal from ARD

Factor	Macingova et al. 2015
Voltage (V)	2.3-2.9
Current (mA)	1000-1600
Anode material	Platinum
Temperature, °C	90°C
pH	0.5-1.0

Methods

Lab Reactors

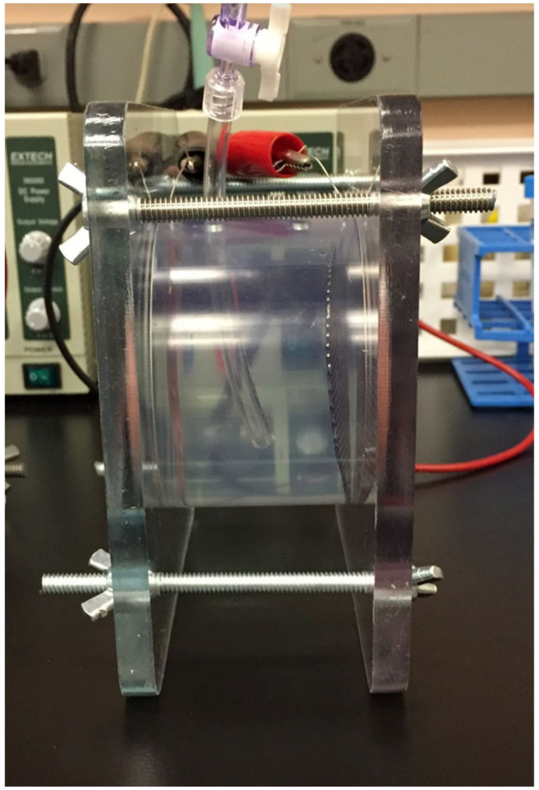
- Clear PVC/acrylic plates
- Glass Beaker
- Cathode (Metal reduction)
    - Cu
    - Metal composite
- Anode (O_2 evolution)
    - Carbon felt
    - Carbon cloth
    - Ti/IrO_2-Ta_2O_5 mesh

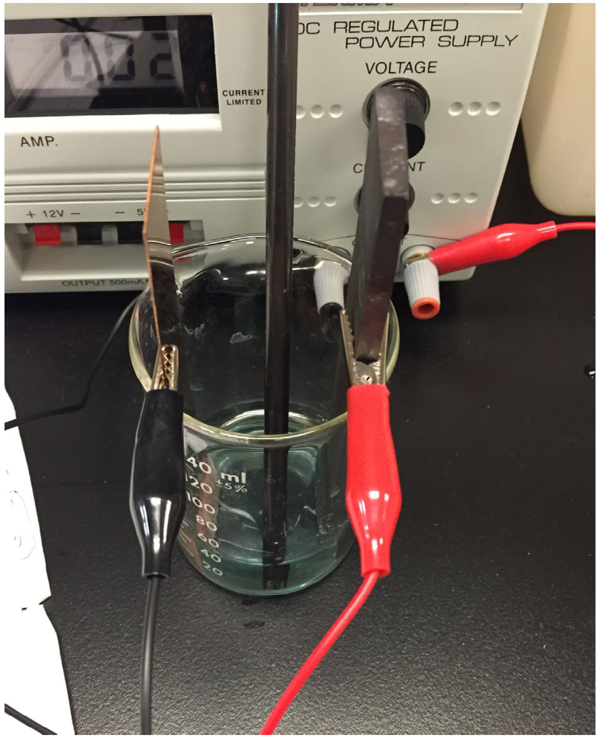
Mine Water

- Argo Tunnel and Virginia Canyon
- Synthetic

Analysis

- ICP
- SEM EDS



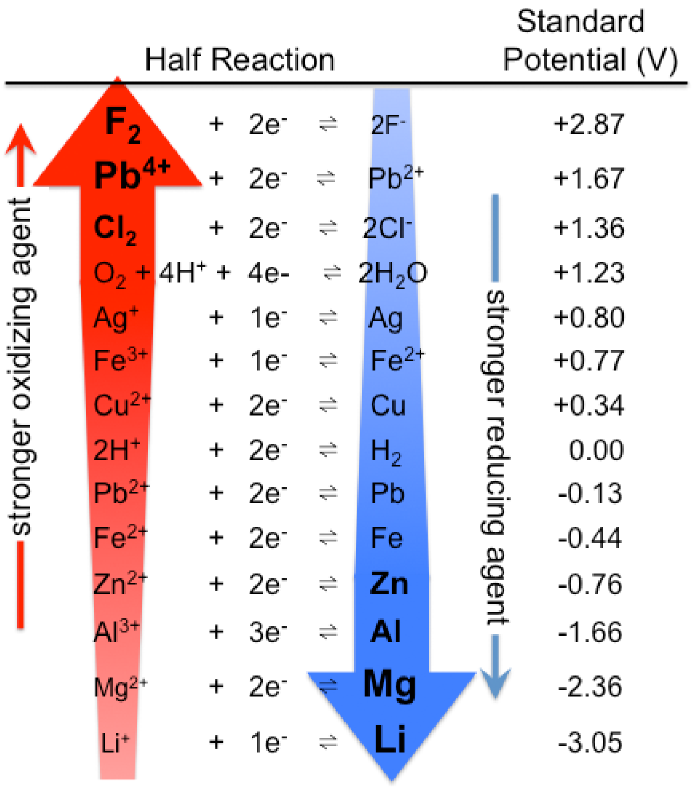


Mine Waters "On-tap" at Argo Tunnel WTP
Idaho Springs, Colorado

Analyte	Virginia Canyon (mg/L)	Argo Tunnel (mg/L)
Al	49	16
Cd	0.31	0.11
Cu	5.9	3.1
Fe	1.9	115
Mn	75	82
Zn	70	42
Sulfate	1885	2009
pH	3.5	3.0

Performance Considerations

- Sequential metal removal
- Electrode composition
- Mine water composition
- Metal deposition
- Efficiency

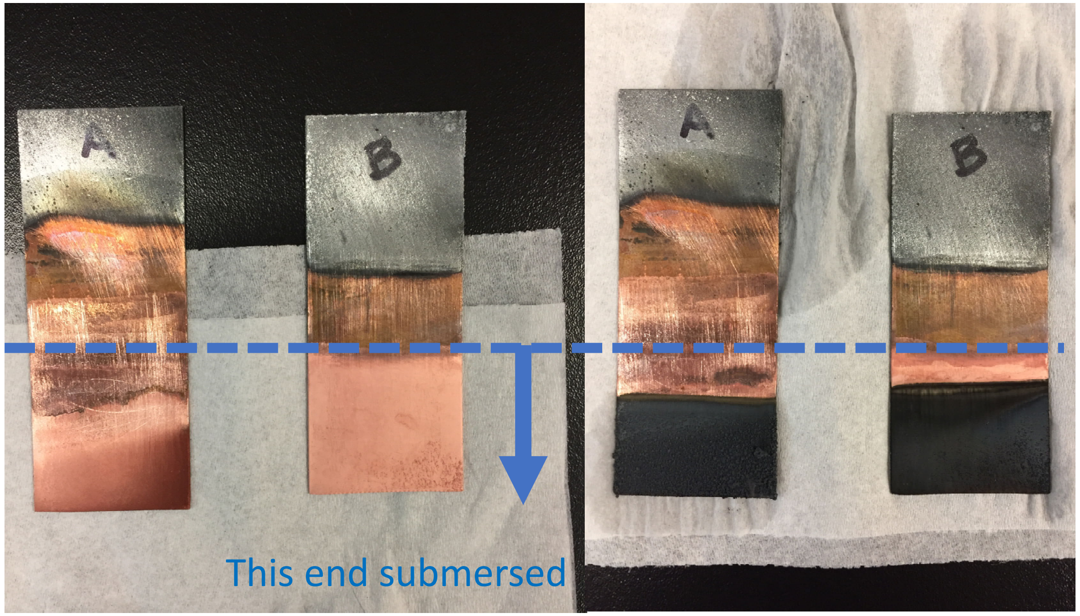


Half Reaction	Standard Potential (V)
$F_2 + 2e^- \rightleftharpoons 2F^-$	+2.87
$Pb^{4+} + 2e^- \rightleftharpoons Pb^{2+}$	+1.67
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36
$O_2 + 4H^+ + 4e- \rightleftharpoons 2H_2O$	+1.23
$Ag^+ + 1e^- \rightleftharpoons Ag$	+0.80
$Fe^{3+} + 1e^- \rightleftharpoons Fe^{2+}$	+0.77
$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+0.34
$2H^+ + 2e^- \rightleftharpoons H_2$	0.00
$Pb^{2+} + 2e^- \rightleftharpoons Pb$	-0.13
$Fe^{2+} + 2e^- \rightleftharpoons Fe$	-0.44
$Zn^{2+} + 2e^- \rightleftharpoons Zn$	-0.76
$Al^{3+} + 3e^- \rightleftharpoons Al$	-1.66
$Mg^{2+} + 2e^- \rightleftharpoons Mg$	-2.36
$Li^+ + 1e^- \rightleftharpoons Li$	-3.05

Sequential Metals Removal

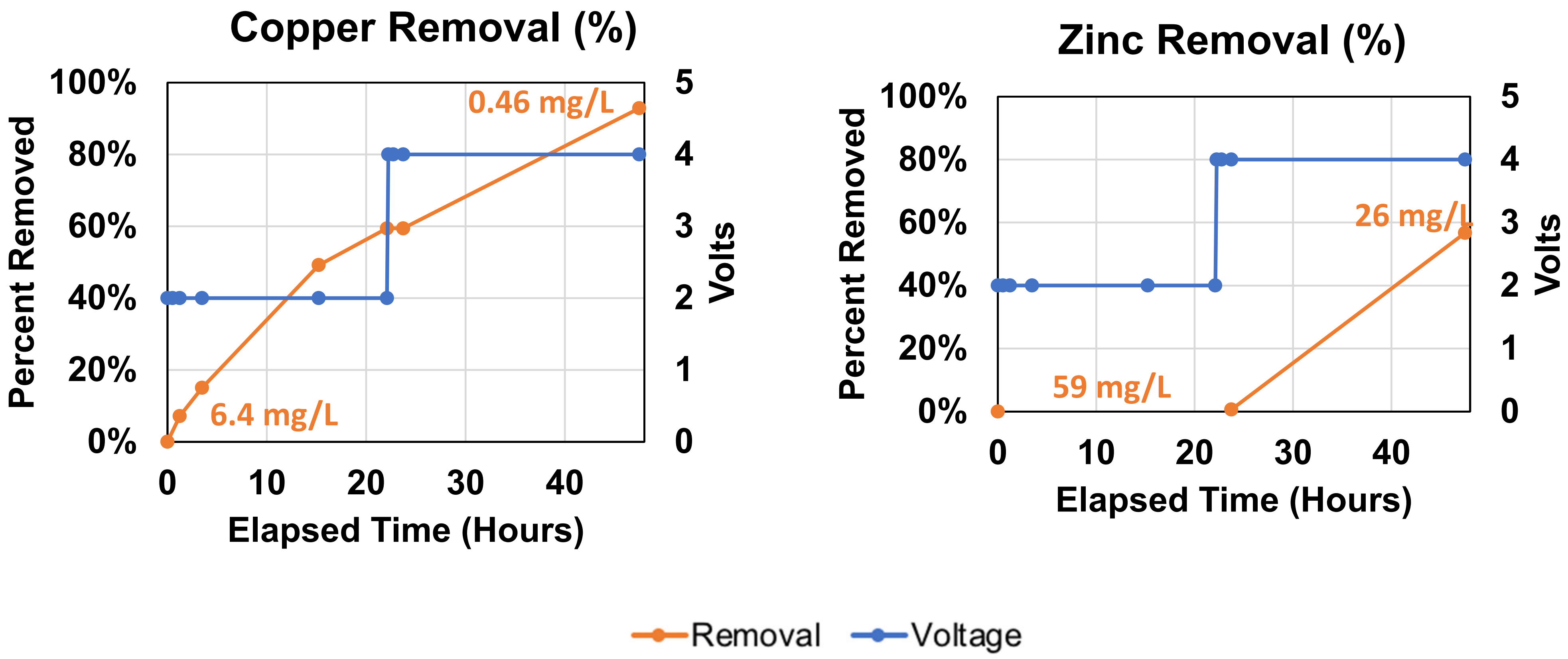
Synthetic Mine Water ($CuSO_4$ and $ZnSO_4$)

Phase 1: Copper Removal (2V)   Phase 2: Zinc Removal (5V)



Sequential metal removal

Virginia Canyon Water



Copper Removal (%)

Zinc Removal (%)

Metal Removal from Low Iron Water

Virginia Canyon Water

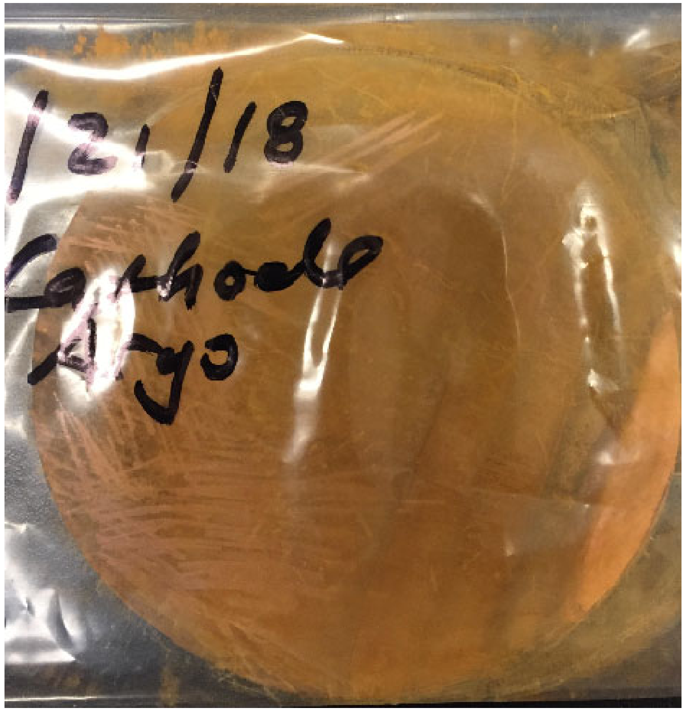
Analyte	Initial Conc.	Anode Type			Max. % Removal
		Carbon Felt 4V	Ti/IrO_2-Ta_2O_5		
			2.8V	5V	
Al	49	27	38	28	44%
Cd	0.31	0.076	0.066	0.035	89%
Cu	5.9	1.3	1.3	0.84	86%
Fe	1.9	0.6	0.45	0.22	88%
Mn	75	40	11	5.3	93%
Pb	0.031	<0.005	<0.005	<0.005	84%
Zn	70	53	67	41	41%
pH	3.5	2.9	2.6	2.5	--

- >80% reduction in dissolved Cd, Cu, and Pb concentrations
- Mn removal 50%-90%
- pH decrease
- Average current efficiency 20%

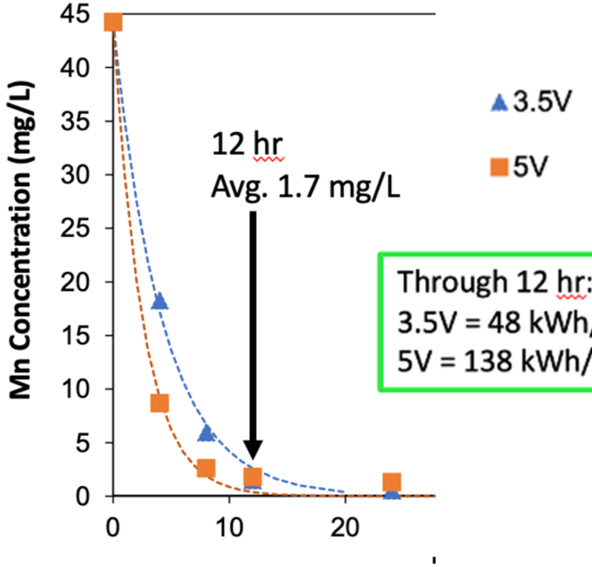
Metal Removal from High Iron Water

Argo Tunnel Water

Analyte	Initial Conc.	Copper Cathode $Ti/IrO_2-Ta_2O_5$ Anode 3.5V	% Removal
Al	16	13	20%
Cd	0.11	0.030	73%
Cu	3.1	1.2	60%
Fe	115	55	52%
Mn	82	87	0%
Pb	0.033	<0.015	55%
Zn	42	41	2%
pH	3.0	2.6	13%



Mn Removal Batch vs Flow-through



12 hr
Avg. 1.7 mg/L

Through 12 hr:
3.5V = 48 kWh/kg Mn
5V = 138 kWh/kg Mn

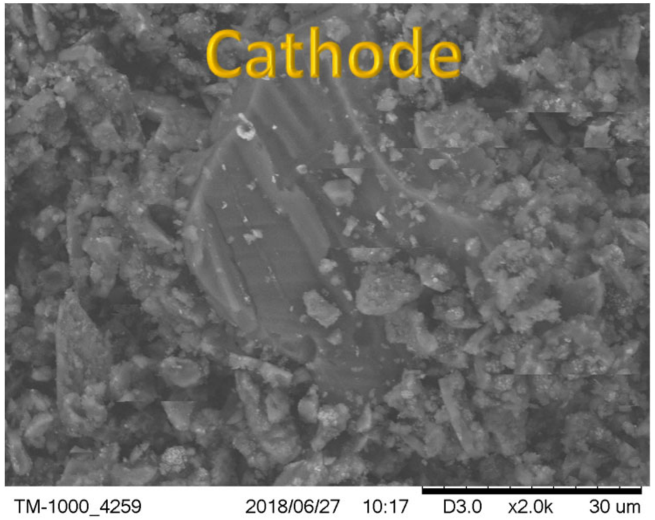
Analyte	Batch Tests			Flow-through Tests		
	Initial	3.5V (12 hr)	5V (12 hr)	Initial	3.5V (Steady State)	3.5V Replicate (Steady State)
Cadmium (mg/L)	0.31	0.024	0.020	0.29	0.14	0.15
Copper (mg/L)	11	0.31	0.61	11	0.6	1.1
Manganese (mg/L)	44	1.5	1.8	43	2.3	2.7
Lead (mg/L)	0.11	<0.02	<0.02	0.11	0.009	0.023
Zinc (mg/L)	33	38	15	31	33	34
pH (s.u.)	2.8	3.1	2.8	3.4	2.8	3.0
1st order rate constant (hr^{-1})		0.24	0.39		1.5	

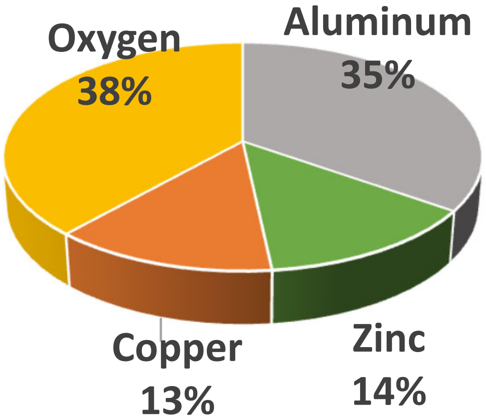
Higher rate of removal in flow-through test due to more efficient mixing

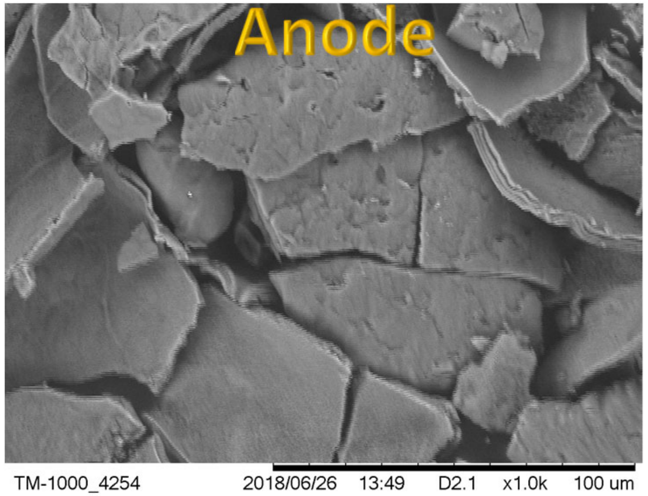
Metals Deposition on Cathode and Anode

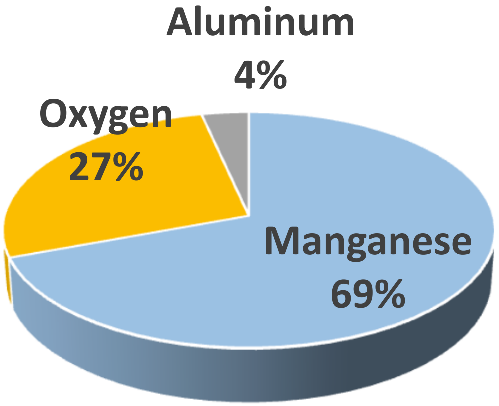
- Cathode
    - Copper
    - Zinc
    - Aluminum
- Anode
    - Manganese
    - Aluminum
- Titanium based electrodes
- Solids Analyzed using SEM-EDS

SEM-EDS =Scanning Electron Microscopy Energy Dispersive X-ray Spectroscopy





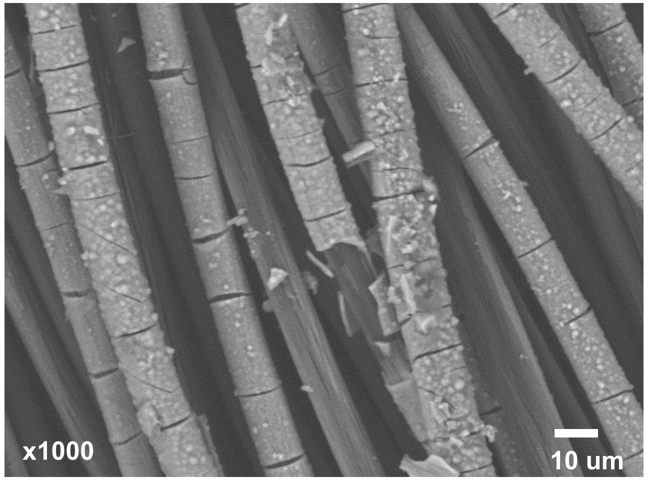




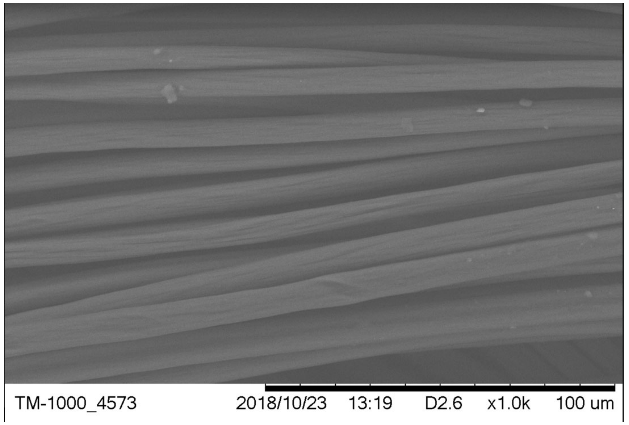
Manganese deposition on carbon electrode

- Anode: carbon cloth coated in Mn and oxygen

  (>90 % MnO_2)
- Cathode: Zn, Cu, and Pb (not shown)



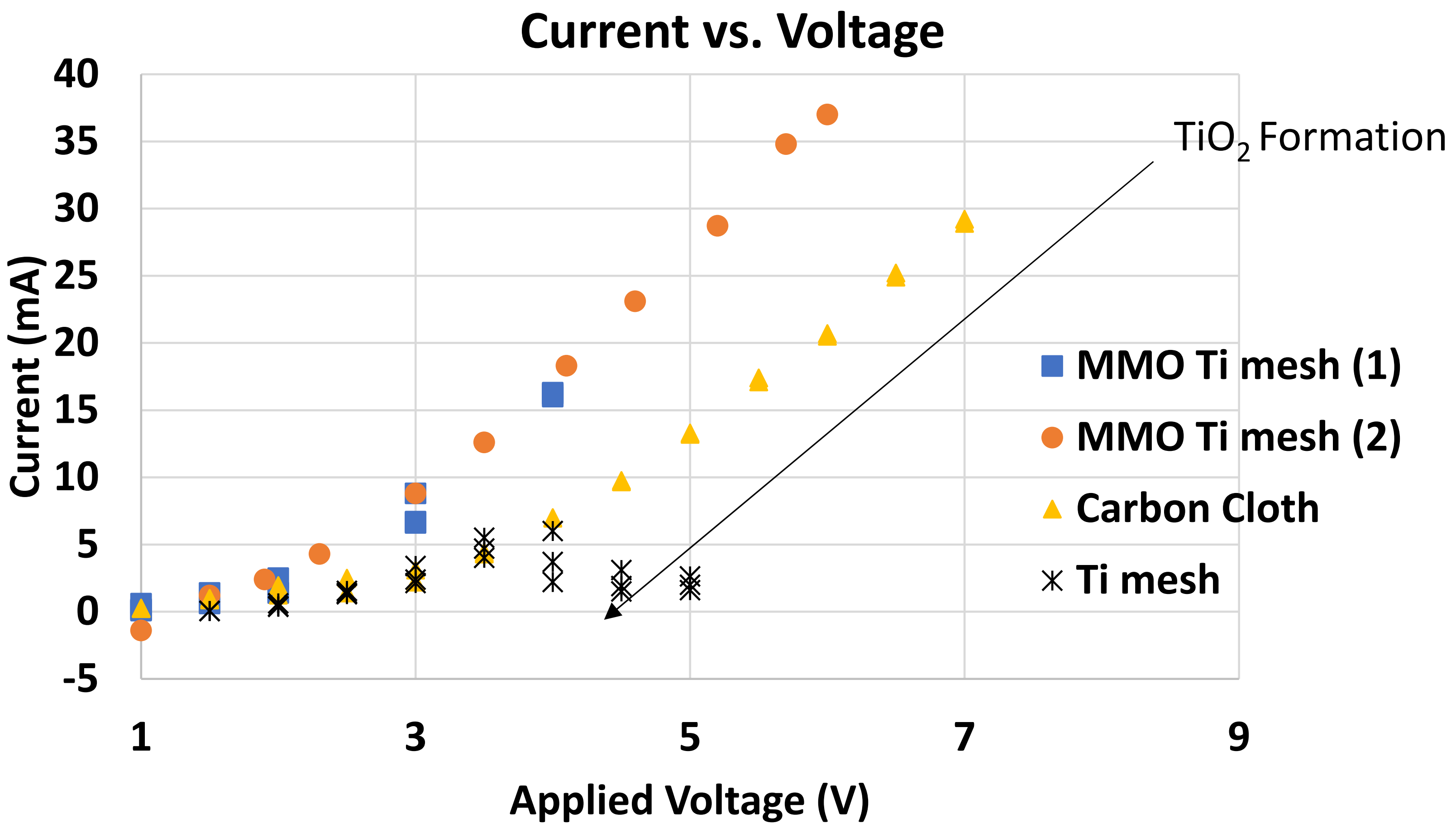
Oxidized manganese coating on carbon cloth fibers



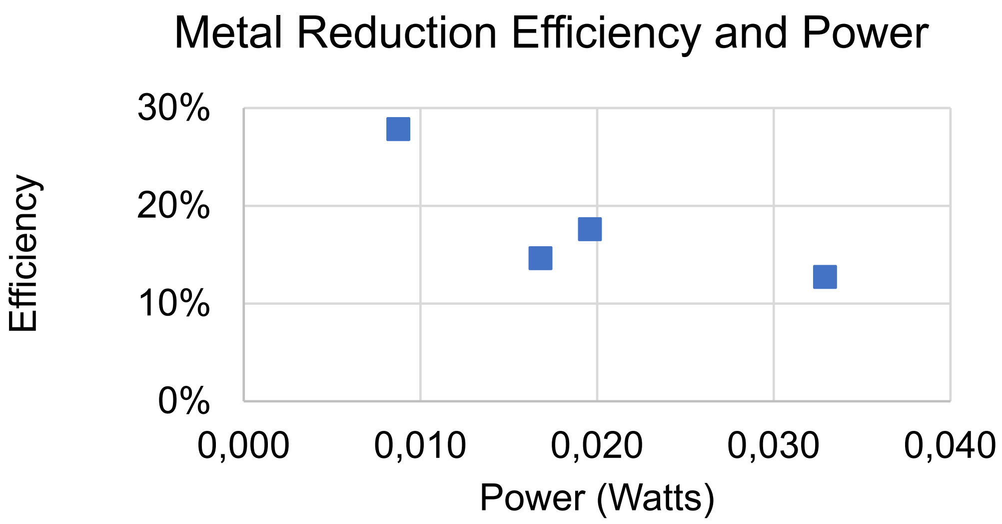
Clean carbon cloth fibers

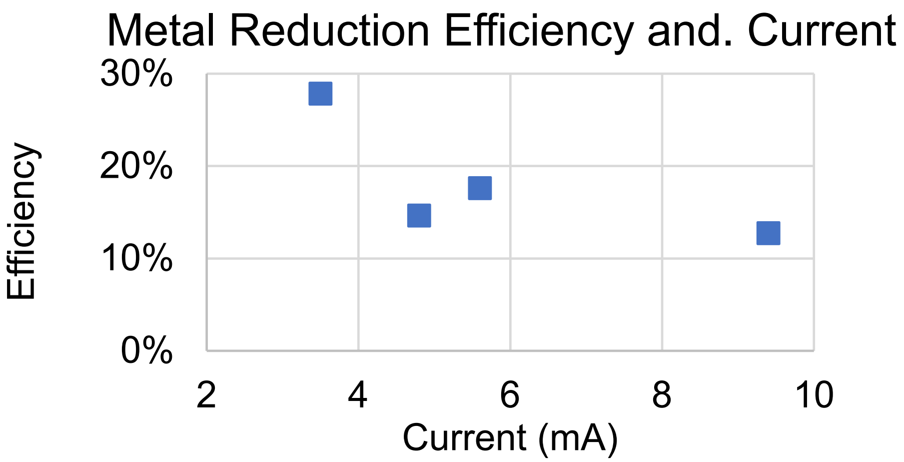
SEM-EDS: scanning electron microscopy with energy dispersive spectroscopy

Current vs. Applied Voltage



Efficiency





- Higher metals reduction efficiency with lower currents.
- Current is affected by mixing, electrode area, and applied voltage.
- Increase in voltage results in minimal increases in metal reduction.

Summary and Implications

- Mn removed at pH 3 on anode
  - Up to 95%
- Concurrently Metals Removed at Cathode
- Electrolytic methods may:
  - Reduce reagent use
  - Reduce sludge volume
  - Provide Mn oxide sorbent
- Methods are more cost-effective than previous studies
- Pretreatment needed for iron rich water
- Optimization needed

Acknowledgements

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