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Passive Treatment of Mine Process Water Using Sulfate-Reducing Bacteria and Biogenic Apatite




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May 9, 2023

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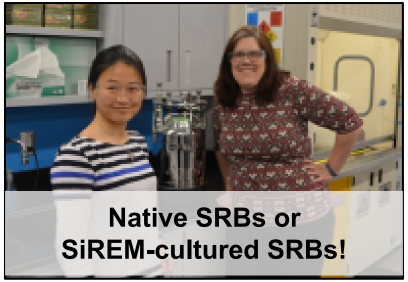
Treatment Goal: Reduce Total Dissolved Solids (TDS) in mine waters impacted with sulfate, metals, and fluoride.



ANAEROBIC RESPIRATOR
Sulfate-reducing Microorganisms (SRBs)

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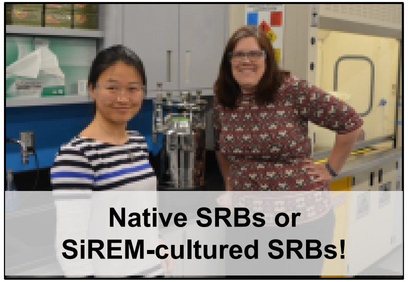

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Sodium lactate, ethanol

ELECTRON DONOR
Organic compounds

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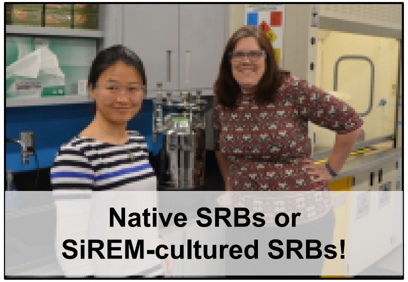

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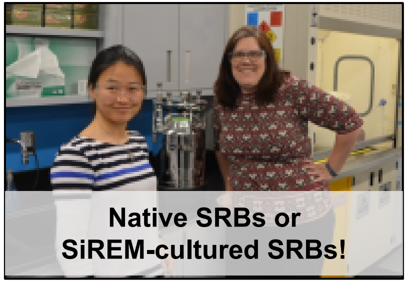

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CARPATITE
Hydroxyapatite*
($Ca_{10}(PO_4)_6(OH)_2 \cdot nH_2O$)

*What is apatite?

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Apatite for destruction

Fish bones are a source of a common mineral that can help us remediate heavy metals, fluoride, and more.

Apatite

- (1) Fluorapatite: $Ca_5(PO_4)_3F$
- (2) Chlorapatite: $Ca_5(PO_4)_3Cl$
- (3) Hydroxyapatite: $Ca_5(PO_4)_3OH$

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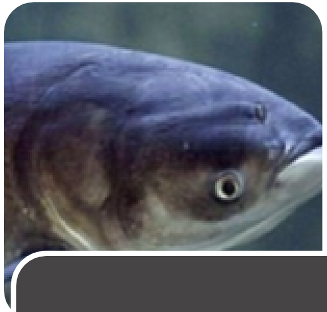
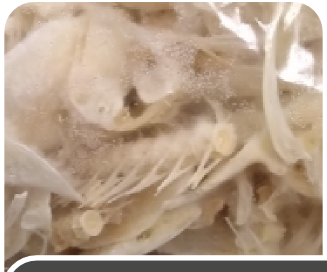


Remove flesh



Wash and Grind

Bake

Apatite for destruction

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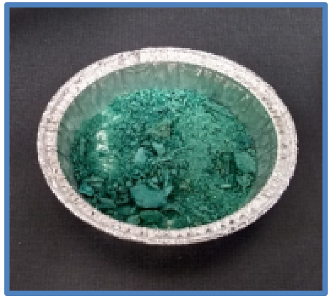
Fish bones before exposure



Fish bones after exposure to dissolved copper solution

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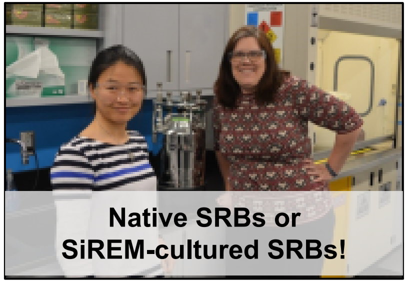

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Mine Research Water

- This mine research water is deep mine shaft water from a mine. It is impacted with sulfate, fluoride, and other components requiring water treatment before discharge.

Main TDS Influences

	Internal analytes in mine research water contributing to TDS (mg/L)										External analytes added and contributing to TDS (mg/L)			Calculated TDS (mg/L)
	Ca	Mg	Na	K	Fe	Mn	HCO_3^-	Cl^-	SO_4^{2-}	SiO_2	Fe	Na	COD (Lactate or ethanol)	
Mine Research Water	300	67	110	31	<DL	3	180	28	1300	--	--	--	--	**2019**

<DL = less than detectable limit

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Next Generation Sequencing (NGS) indicated a diverse community of organisms.

Even though the functional group of sulfate reduction was only 0.06% abundant, we were still able to stimulate those microorganisms.

Functional Group	Percent Abundance
Chemoheterotrophy	18.21%
Methylotrophy	15.14%
Methanotrophy	12.79%
Hydrocarbon Degradation	12.79%
Photoautotrophy	6.17%
Phototrophy	6.17%
Photosynthetic Cyanobacteria	6.04%
Oxygenic Photoautotrophy	6.04%
Nitrification	4.07%
Aerobic Ammonia Oxidation	2.66%
Aerobic Chemoheterotrophy	2.44%
Methanol Oxidation	2.35%
Aerobic Nitrite Oxidation	1.42%

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Column performance after 7 weeks of flow through

With regards to:

- pH
- Fluoride
- Final TDS Considerations

Column Performance

pH over seven weeks

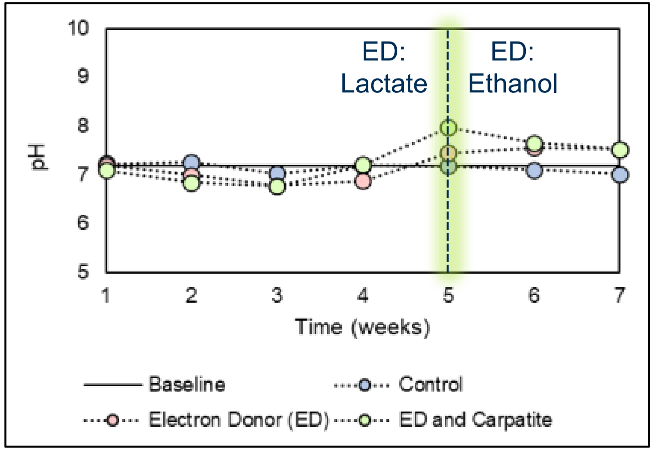
- Sulfate reduction does generate more alkaline conditions though the severity of this shift can be managed by the selection of the electron donor.

Lactate as electron donor:

$$2C_3H_5O_3^- + 3SO_4^{2-} + \mathbf{8H^+} \rightarrow 3H_2S + \mathbf{6CO_2} + 6H_2O$$

Ethanol as electron donor:

$$2C_2H_6O + 3SO_4^{2-} + \mathbf{6H^+} \rightarrow 3H_2S + \mathbf{4CO_2} + 6H_2O$$



Column Performance

Fluoride levels over seven weeks

	Fluoride (mg/L)							
	t=0	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6	Week 7
Baseline	3.2	--	--	--	2.5	2.6	2.7	--
Control	--	--	3.4	2.9	2.6	2.7	2.8	2.2
Electron Donor (ED)	--	--	2.1	2.2	2.5	2.3	2.4	2.9
ED and Carpatite	--	--	<DL	<DL	<DL	<DL	<DL	<DL

Carpatite successfully removed the fluoride from the mine water.

Column 1: Mine water (Control)

Column 2: Mine water +lactate or ethanol

Column 3: Mine water, +Lactate or ethanol, and Carpatite

<DL = less than detectable limit

Conclusions

	Internal analytes in mine research water contributing to TDS (mg/L)										External analytes added and contributing to TDS (mg/L)			Calculated TDS (mg/L)
	Ca	Mg	Na	K	Fe	Mn	HCO_3^-	Cl^-	SO_4^{2-}	SiO_2	Fe	Na	COD (Lactate or ethanol)	
Mine Research Water	300	67	110	31	<DL	3	180	28	1300	--	--	--	--	**2019**
Control	250	55	100	26	<DL	21	160	<DL	1031	42	--	--	--	**1685**
Electron Donor (ED)	210	60	110	27	<DL	1	310	<DL	592	39	1	10	718	**620**
ED and Carpatite	300	68	110	30	<DL	1	560	<DL	318	51	<DL	10	639	**789**

<DL = less than detectable limit

May **increase** over the operation of the column as **sulfate reduction introduces carbonate** into the system.

*Will continue to **decrease** over the operation* of the column.

Any ***increase*** is a result of steel wool added to the column to *neutralize hydrogen sulfide*.

Sodium lactate selected as e^- donor.

This value will change based on pilot scale use of ethanol, methanol, EVO, or high fructose corn syrup.

This value will continue to be optimized.

High value indicates overfeeding of the bacteria.

Ideally, this value is zero.

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Highlights and Takeaways

- Biological component in study
  - Atypical to be included in mine water projects
  - Next Generation Sequencing (NGS) can be used to:
    - Understand dominant and potential microbial processes
    - Determine the impact of electron donors, nutrients, pH buffers, bioaugmentation
    - Identify inhibitory conditions and challenging site locations
    - Make informed decisions to manage bioremediation
- Initial proof-of-concept study
  - Evaluated if proposed technologies could be used to mitigate site issues
  - results indicate ***yes***, *but requires fine-tuning*

Future Directions

- Additional studies to optimize/range find conditions to reduce sulfate & TDS
- New study under **thermophilic** conditions
  - The **ambient temperature** of mine water at the site is ***80°C***
  - *Previous study* occurred under **<u>mesophilic/room temperature</u>** conditions (22°C)
  - Provides an opportunity to use a thermophilic reaction with limited input of additional energy to heat the water
  - Opportunity to study native thermophilic SRB community
  - ***Will sulfate reduction still occur? How will the rate of sulfate reduction be affected relative to mesophilic conditions?***
- Microcosm study to determine ideal temperature for sulfate & TDS reduction → column work to optimize mesophilic or thermophilic incubation conditions
- Carpatite worked very well for resolving fluoride in the water and will be used in pilot scale system!

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Questions?

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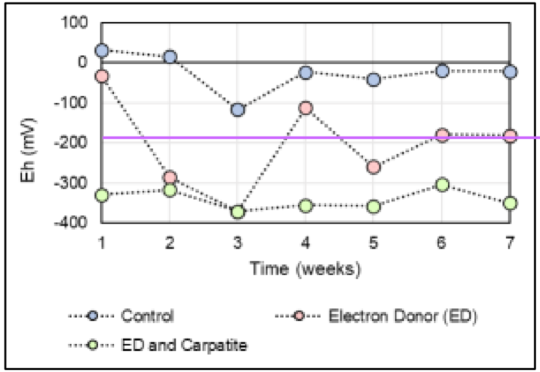
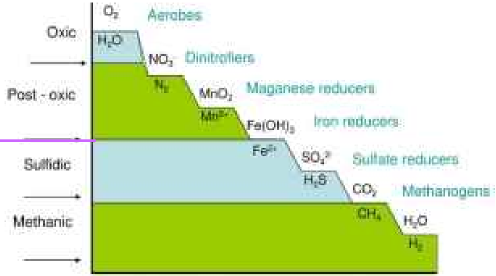
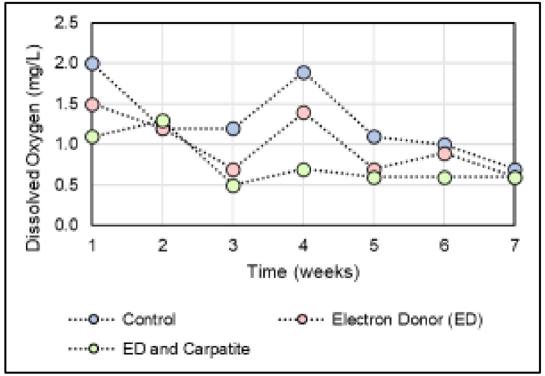
Column Performance

Redox







Experimental columns retained reduced conditions over the experiment.

The column ammended with fish bone remained highly reduced.

Column Performance

Sulfate and Fluoride

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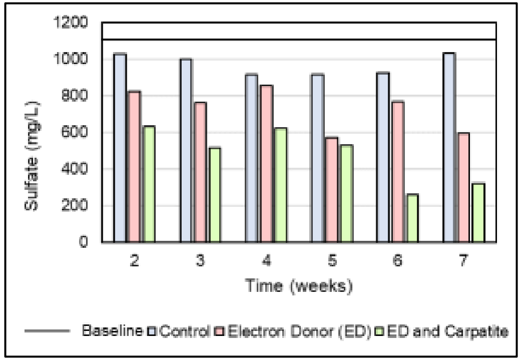
ED and Carpatite	--	--	0	0	0	0.1	0	0



	Sulfate (mg/L)	
	t=0	Week 7
Baseline	1300	--
Control	--	1031
Electron Donor (ED)	--	592
ED and Carpatite	--	318