Low-concentration Sulfate Removal from Wastewater with Barite Precipitation Technology

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Low-concentration sulfate removal from wastewater with barite precipitation technology

Meijun Cai, Sara P. Post, Shashi Rao, Chan Lan Chun,
Lucinda Johnson, and George Hudak

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Sulfate Regulations

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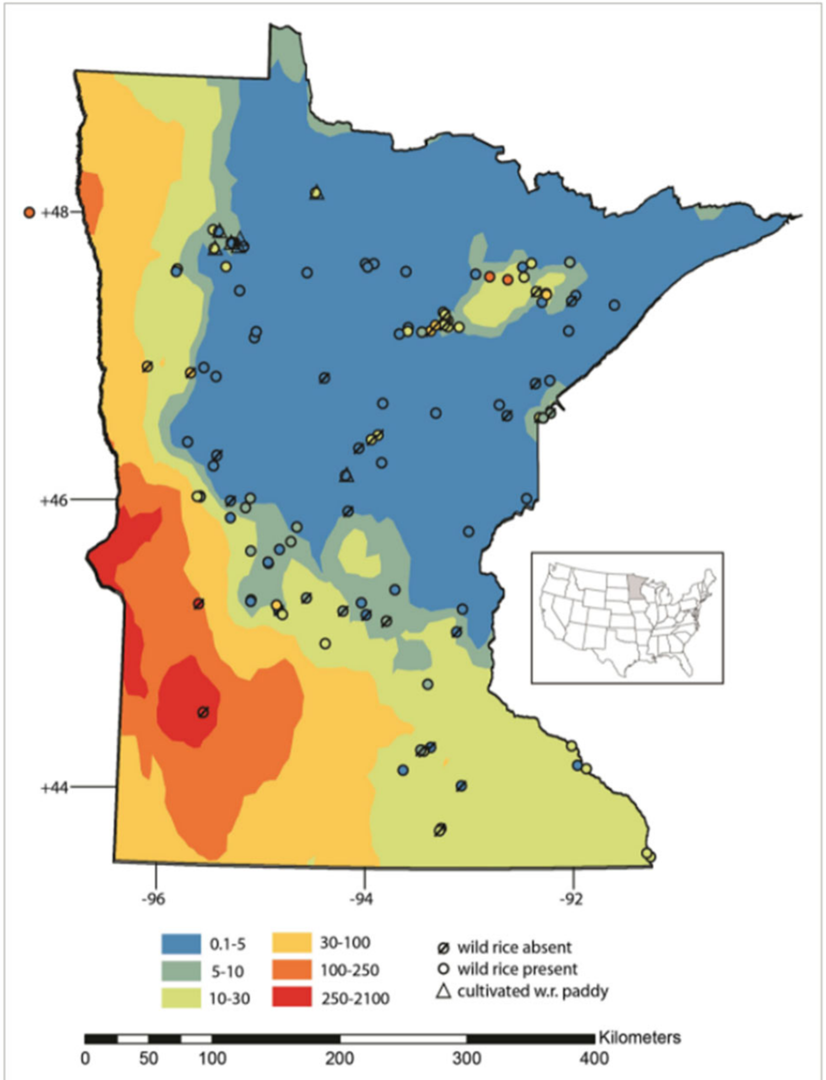
EPA Drinking Water Standard (secondary)

250 ppm

Minnesota regulation for wild rice waters

10 ppm

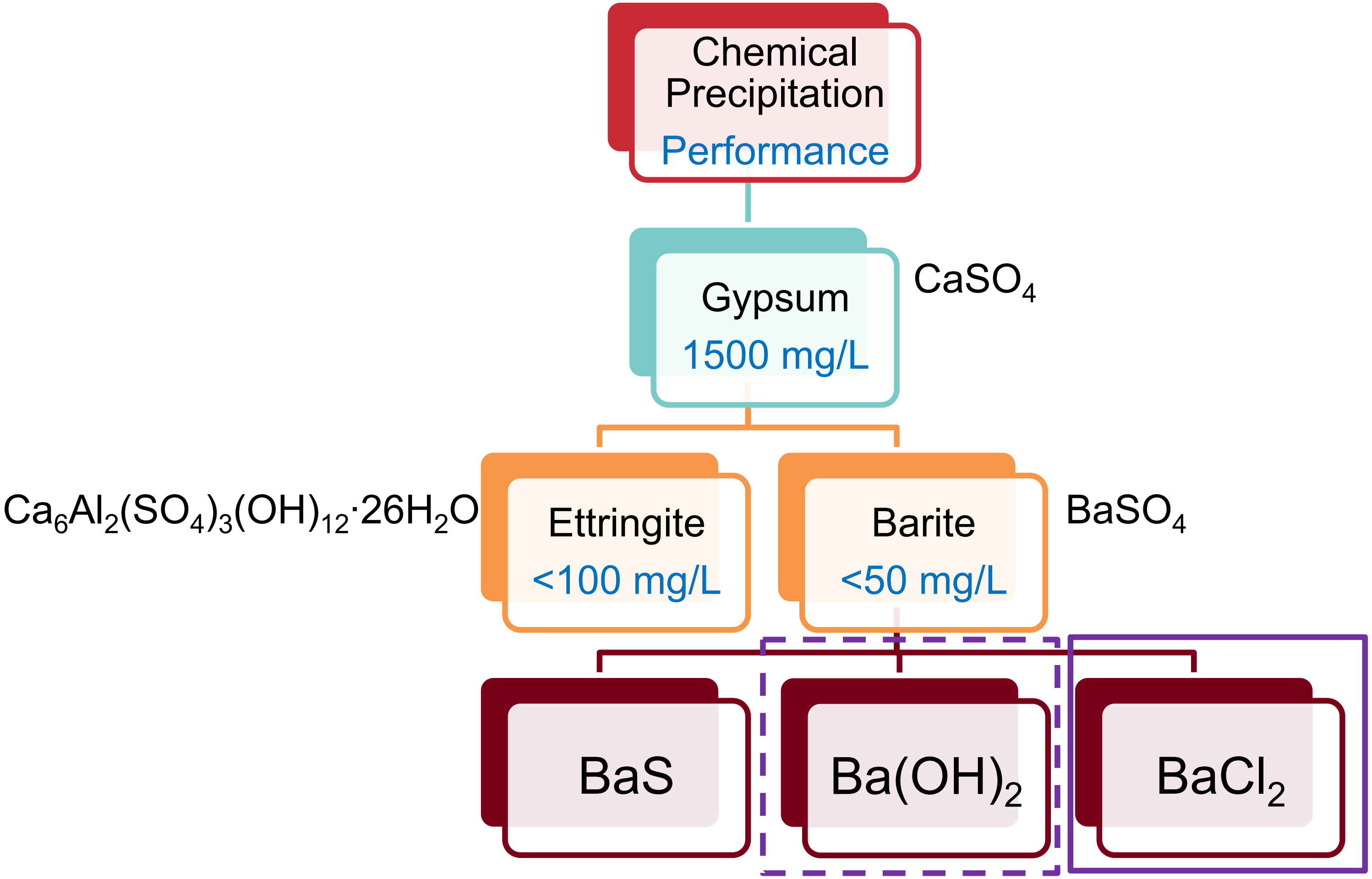
Sulfate in Minnesota



- 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.

Potential Chemical Precipitation Technologies



Reference: Bolton & Menk., Inc., (2018). Analyzing Alternatives for Sulfate Treatment in Municipal Wastewater. https://www.pca.state.mn.us/sites/default/files/wq-rule4-15pp.pdf

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Laboratory Chemical Precipitation Tests

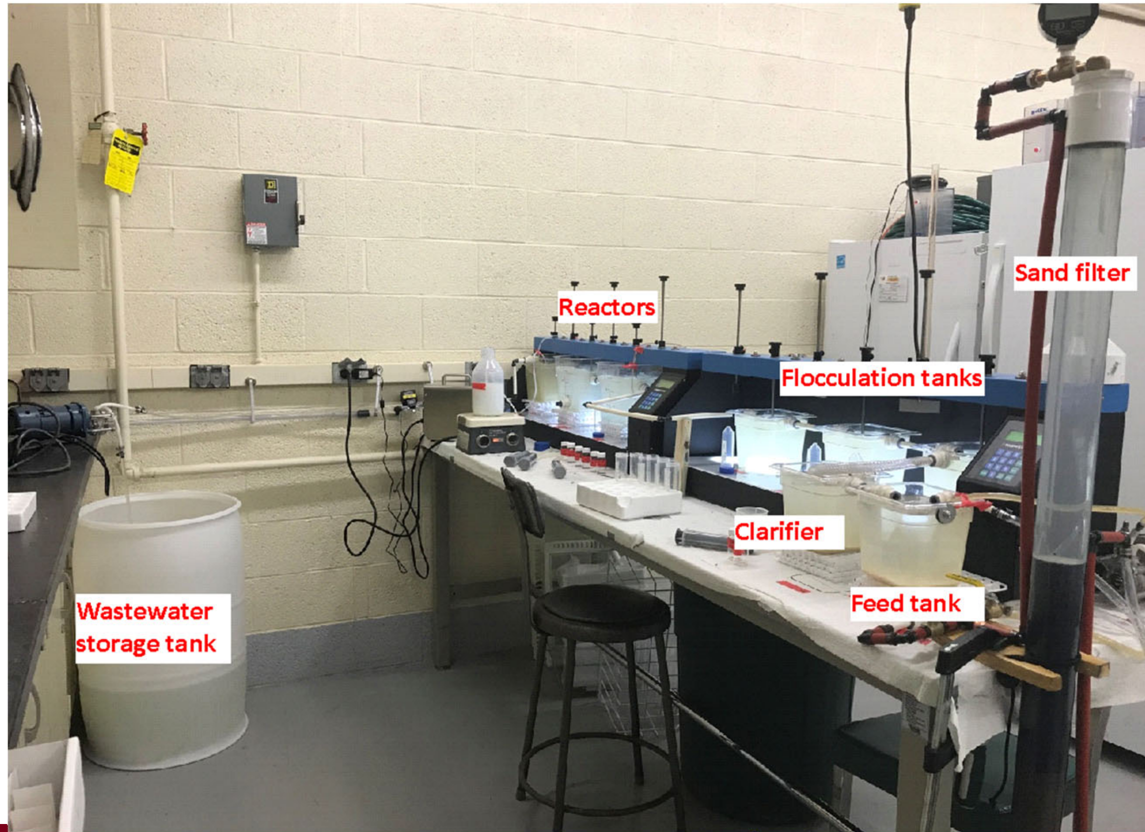
Batch tests and bench-scale continuous tests to test to setup the process parameters

Municipal wastewater tested

- Plant 1: 60 mg/L
- Plant 2: 80-120 mg/L
  with chelating organics
- Plant 3: 200-300 mg/L
- Plant 4: 200-400 mg/L

Other water tested

- One tap water, 300-400 mg/L
- A mine pit lake water, 300-400 mg/L



Laboratory Parameters Tested

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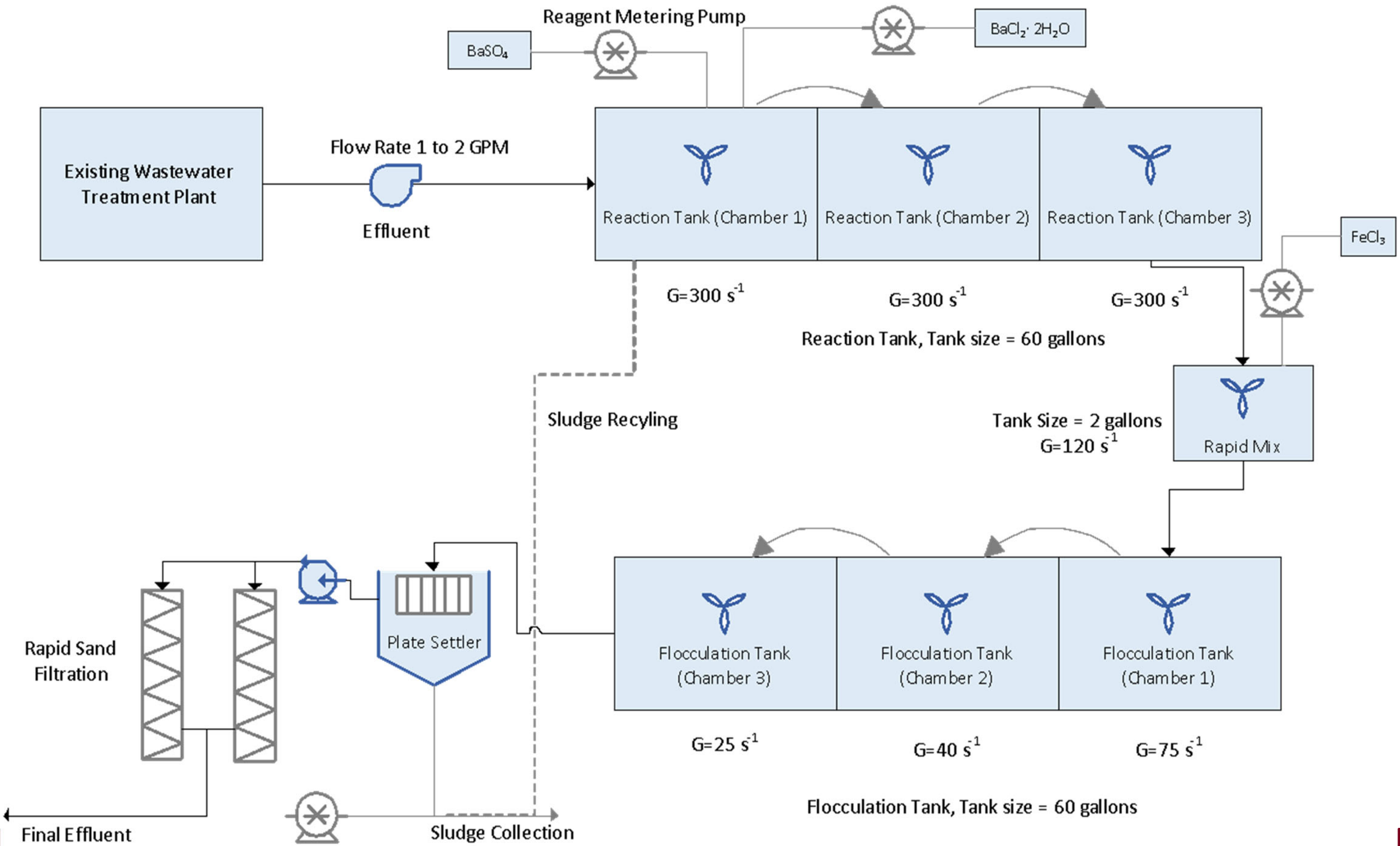
Precipitation reaction related:

1. Residence time: 5, 10, 15, 20, 25, 30 min, 1, 2, 4, 6.5 and 24 hours
2. Mixing rates: 150 rpm, 300 rpm
3. Seed ($BaSO_4$) dosage rates: 0.1, 0.6, 1 g/L
4. Overdose rates of $BaCl_2$ (molar ratio of $Ba:SO_4$): 1, 1.1, 1.2, 1.3, 1.4, 1.5
5. Temperature: 4°C, 20°C

Flocculation related:

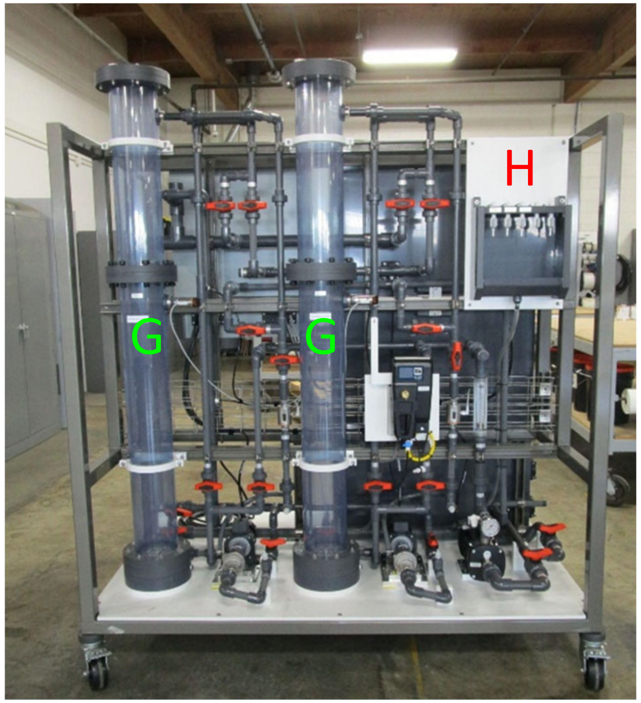
1. Flocculant types: $FeCl_3$, Alum, organic polymers (C-577, C-592, A-1849Rs, N-100)
2. Flocculant dosage rates (mg/L): 0, 0.1, 0.2, 0.5, 1, 2, 2.5, 4, 5, 10, 20, 25, 50, 100


Reagent Metering Pump
$BaSO_4$
$BaCl_2 \cdot 2H_2O$
Existing Wastewater Treatment Plant
Flow Rate 1 to 2 GPM
Effluent
Reaction Tank (Chamber 1)
Reaction Tank (Chamber 2)
Reaction Tank (Chamber 3)
$FeCl_3$
G=300 s^{-1}
G=300 s^{-1}
G=300 s^{-1}
Reaction Tank, Tank size = 60 gallons
Sludge Recyling
Tank Size = 2 gallons
G=120 s^{-1}
Rapid Mix
Rapid Sand Filtration
Plate Settler
Flocculation Tank (Chamber 3)
Flocculation Tank (Chamber 2)
Flocculation Tank (Chamber 1)
G=25 s^{-1}
G=40 s^{-1}
G=75 s^{-1}
Flocculation Tank, Tank size = 60 gallons
Final Effluent
Sludge Collection

Flocculation and Sedimentation Modules

A - Reaction Tank; B - Flocculation Tank; C - Sedimentation Tank; D - Sludge Holding Tank; E- Chemical Dosing Pumps; F - Chemical Storage Tanks

Filtration Module and Trailer



G - Filtration Columns; H - Backwash Tank

8.5 x 20 ft trailer

Field Pilot Trial in 2021(3.5 months)

Wastewater Treatment Plant 1

Domestic wastewater only

Sulfate level: ~60 ppm

Wastewater Treatment Plant 2

Domestic + Industrial wastewater (contain chelating organics)

Sulfate level: 85-115 ppm

Field Pilot Trial in 2022 – 8 weeks

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<u>Domestic wastewater</u>

Sulfate level: 180-250 ppm

<u>Tap water</u>

Sulfate level: 300-350 ppm

SO_4 Concentrations in Effluent

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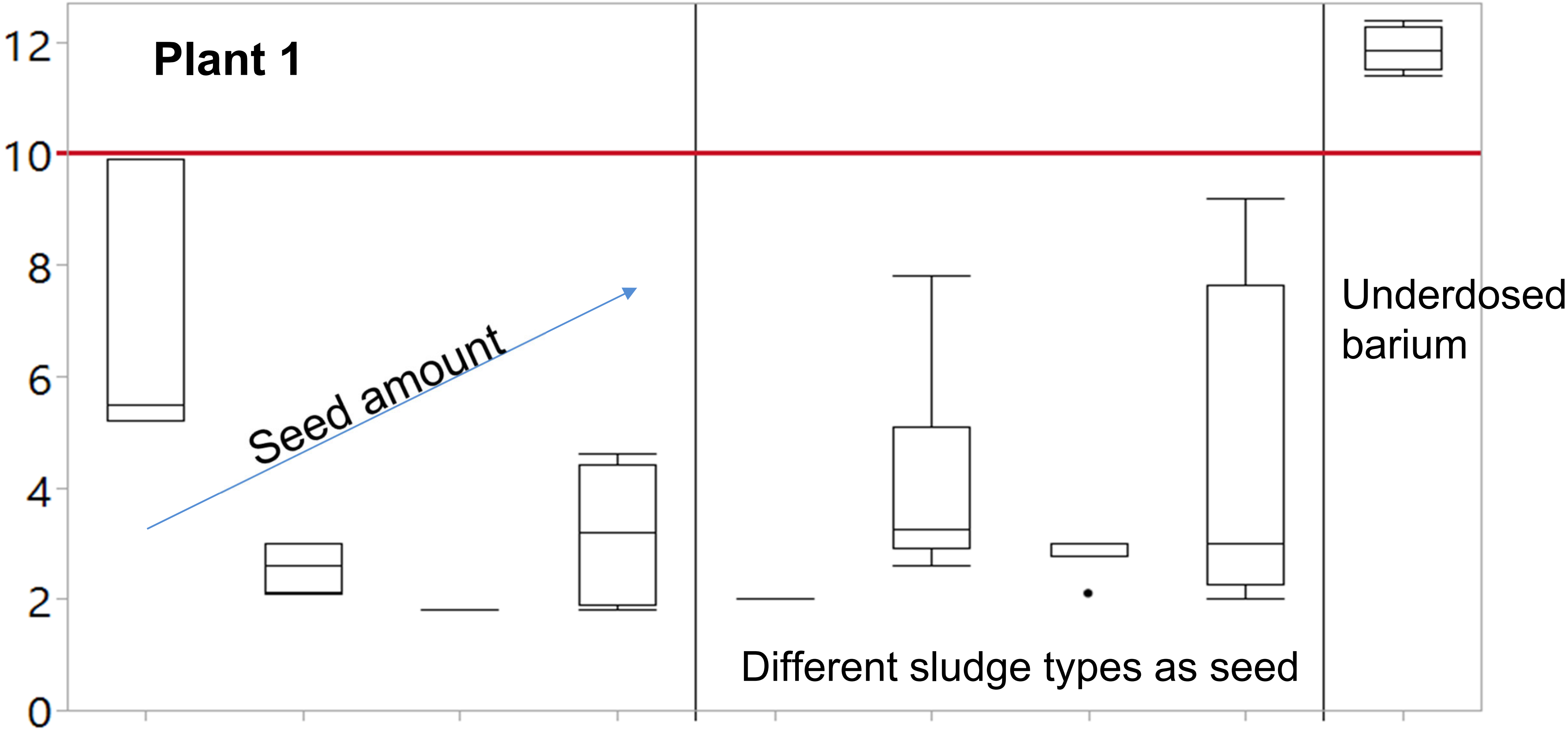

SO_4 Concentrations in Effluent

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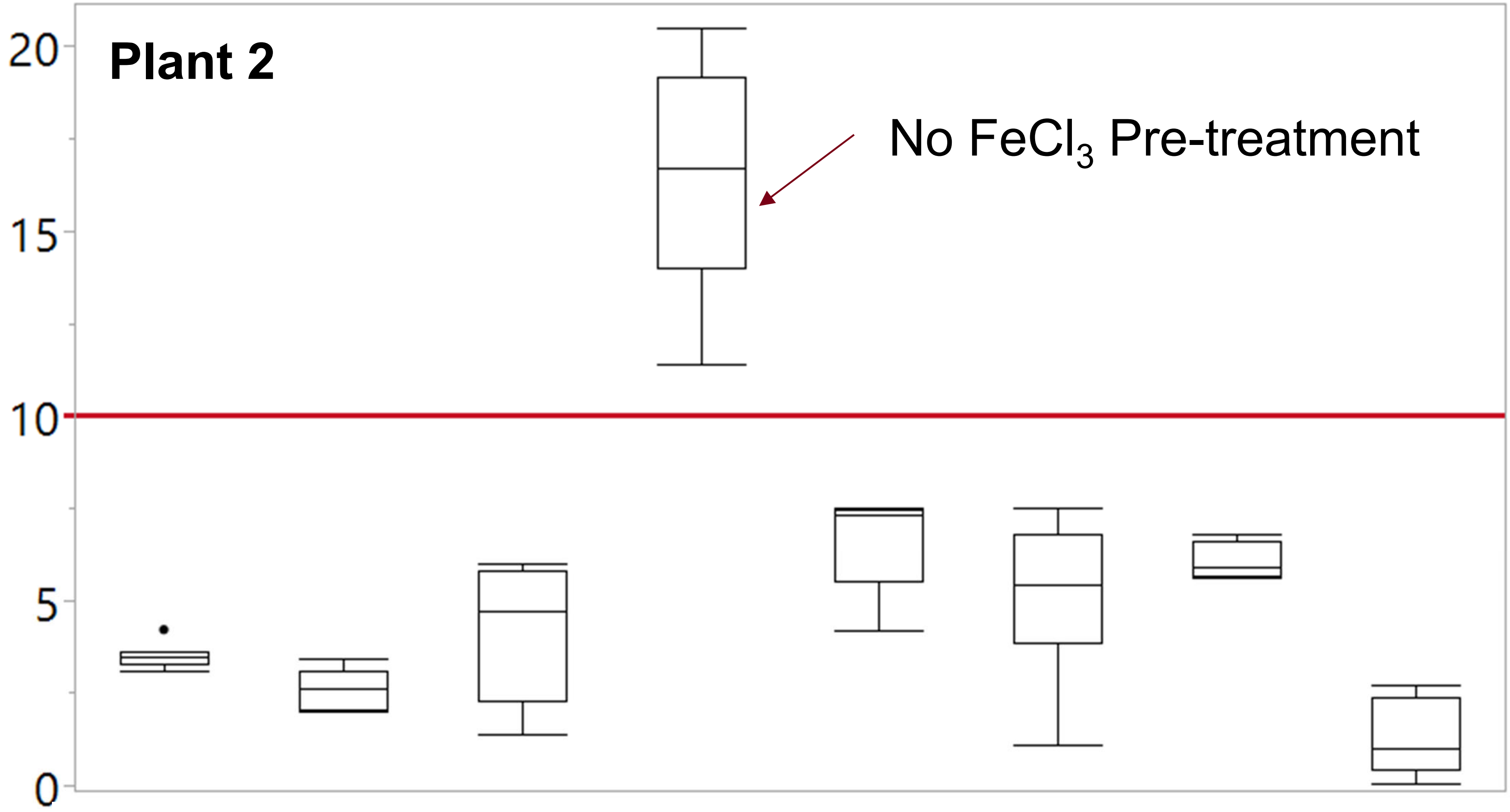


Different Seed Type, Amount, and Pretreatment $FeCl_3$ Amount

Plant 3

Influent water type	Influent concentration, mg/L		Effluent concentration, mg/L			Molar ratio of Ba:SO_4
	SO_4^{2-}	$BaCl_2 \cdot 2H_2O$ added	SO_4^{2-}	Cl^-	Ba^{2+}	
Wastewater	214	700	2.23	323	63.65	1.31
	185	200	98.55	122	0.25	0.92
	224	500	45.83	277	0.45	1.11
	230	100	141	142	0.10	0.44
	226	600	2.64	341	17.18	1.06
	260	350	120	218	0.11	0.97
Tap water	342	850	37.36	271	0.49	1.10
	373	400	194	148	0.05	0.88

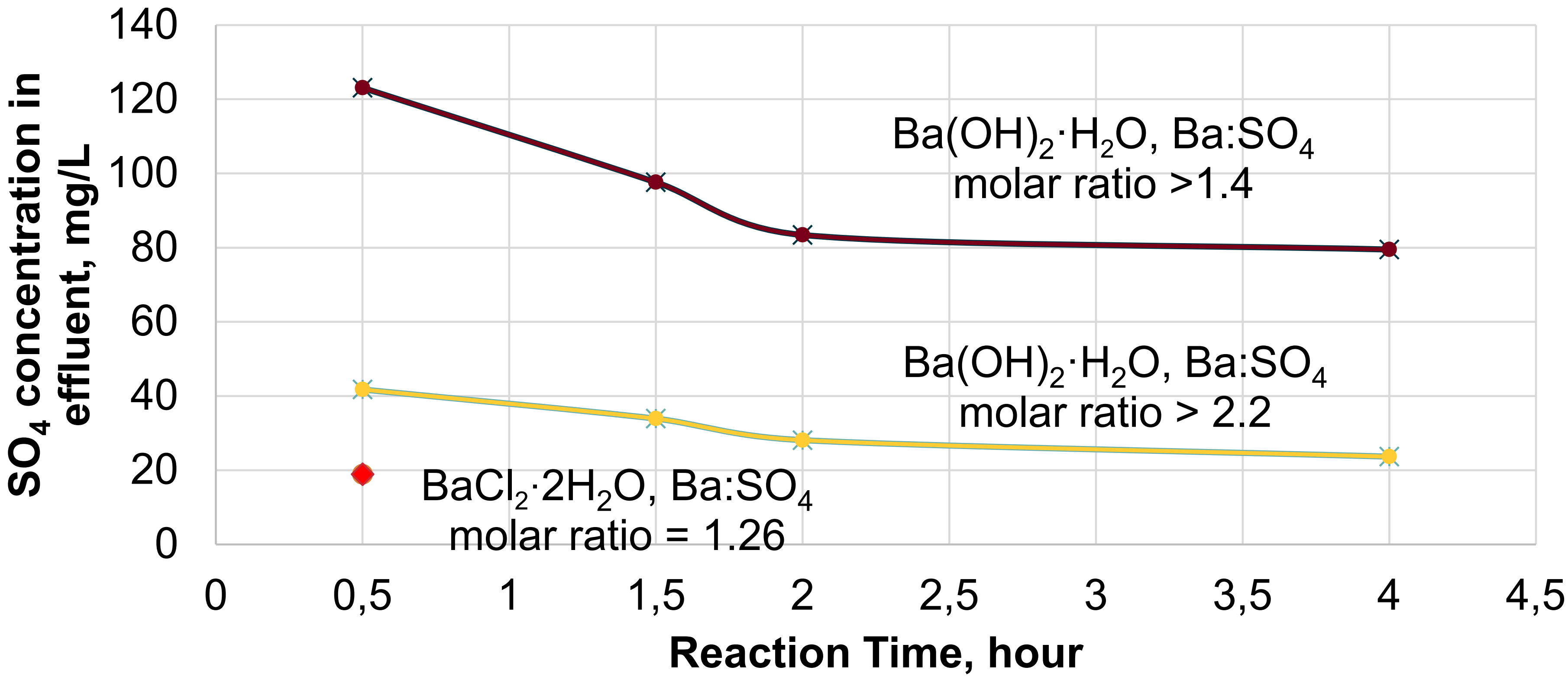
Issues – Effluent Water Quality

- Overdose of barium chemical in order to achieve 10 mg/L
  - Free barium in the effluent, up to 20 mg/L
- High chloride concentrations in effluent
  - Increase 75 mg/L of chloride while reducing 100 mg/L of sulfate

Chemical	Primary drinking water standard, mg/L	Secondary drinking water standard, mg/L	Recreational water standard (class 2), mg/L
Ba^{2+}	2		
Cl^{-}		250	230

Solutions for Chloride in Effluent

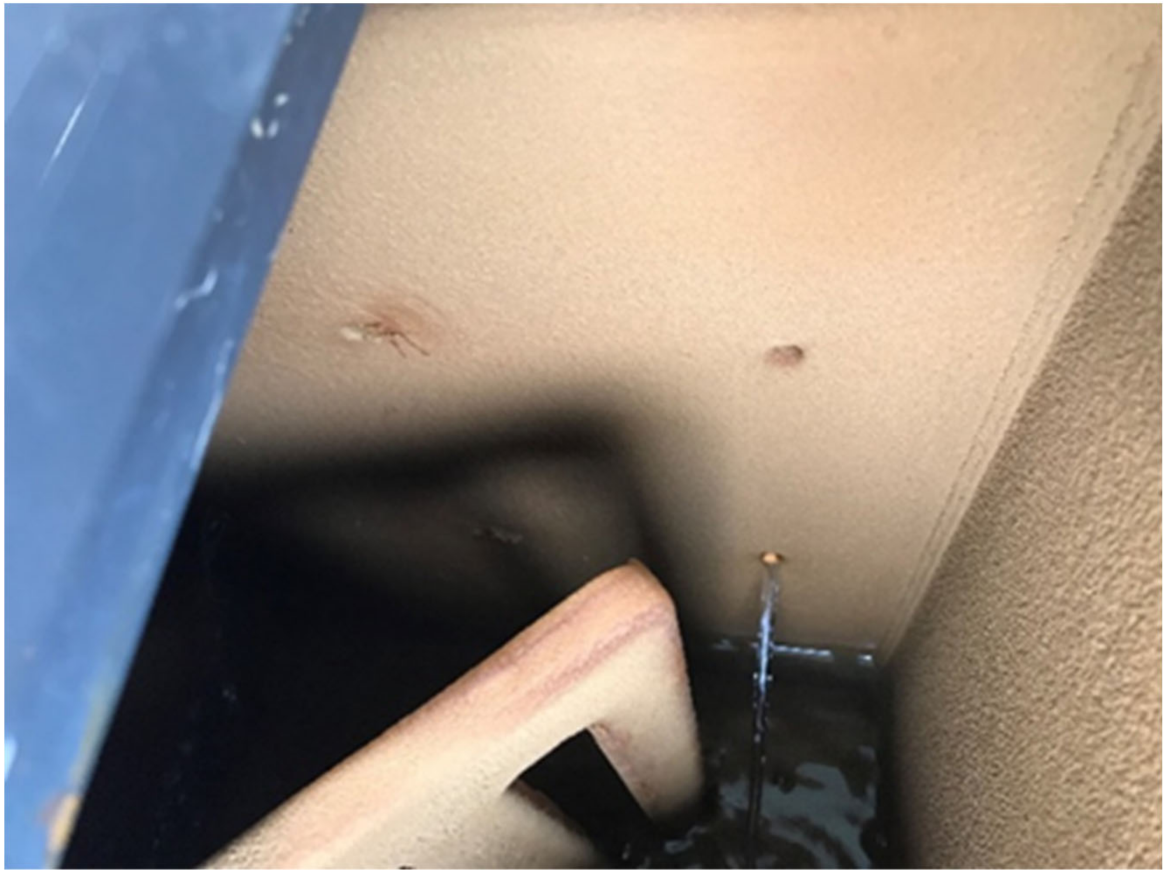
- Add ion exchange to remove chloride
- Use $Ba(OH)_2$ instead of $BaCl_2$, plus CO_2 neutralization



Issues - Process

- Seed is required if influent sulfate concentrations are below 100 mg/L
  - Sludge can be recycled as seed
- Chelating organics in wastewater inhibit the precipitation reaction
  - Pre-treat with ferric chloride to remove organics
- Large amount of sludge produced
  - Exploring the potential use of the sludge
    - Drilling fluid?
    - Construction material for radiation room?
- System treats a single chemical only
  - Exploring the co-treatment of phosphate and mercury

More issues - Scale



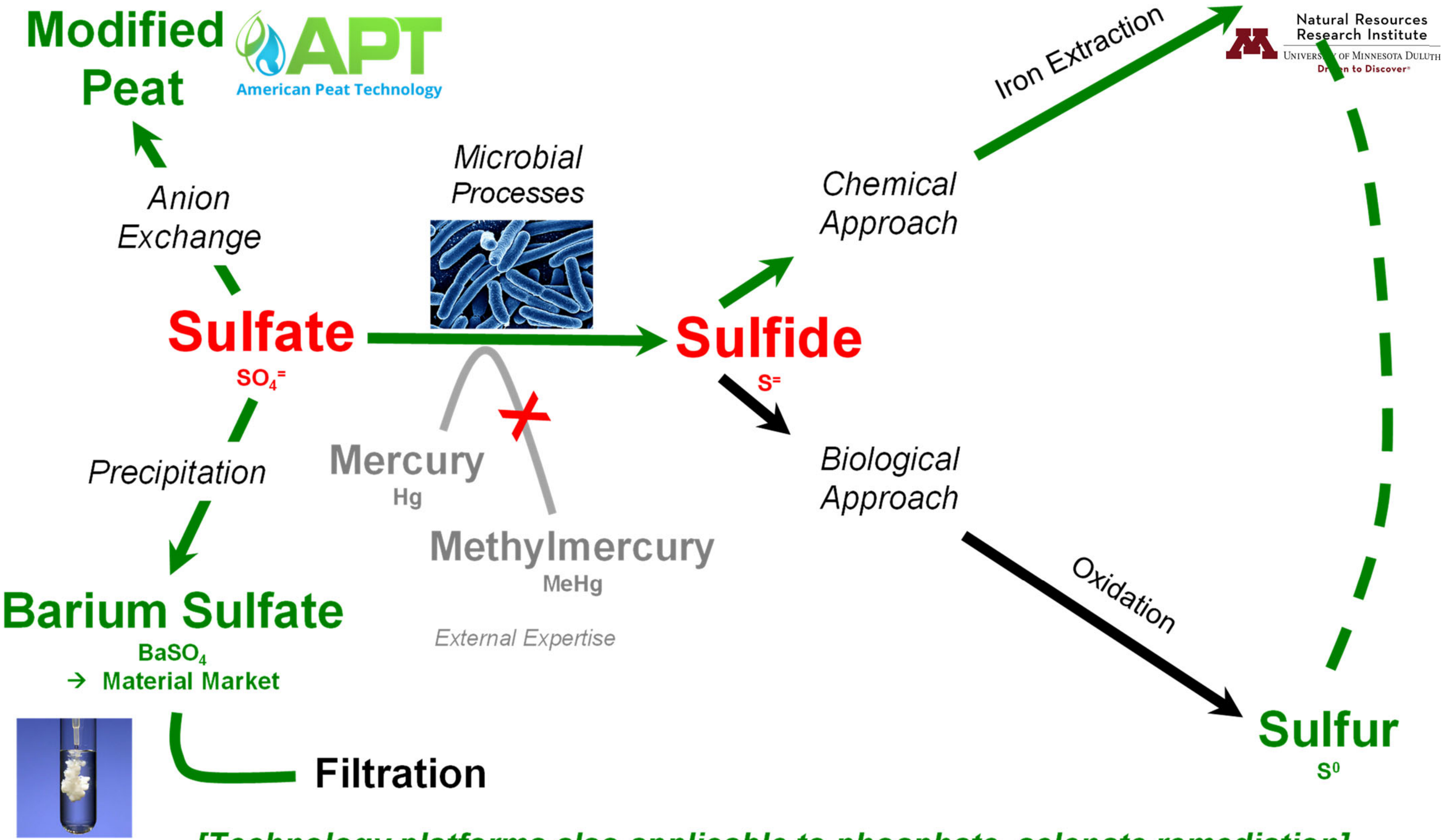
- At our first WWTP in the 2021 field trials, we encountered an unexpected scale issue
- At our second WWTP, we learned that $FeCl_3$, which we added to address chelating organics, also appeared to dramatically reduce the scale buildup
- So, could we use $FeCl_3$ just to address scale? If so, how much would we need?

Adding $FeCl_3$ prior to reaction

$FeCl_3$ = 20 mg/L

$FeCl_3$ = 50 mg/L

$FeCl_3$ = 100 mg/L



[Technology platforms also applicable to phosphate, selenate remediation]

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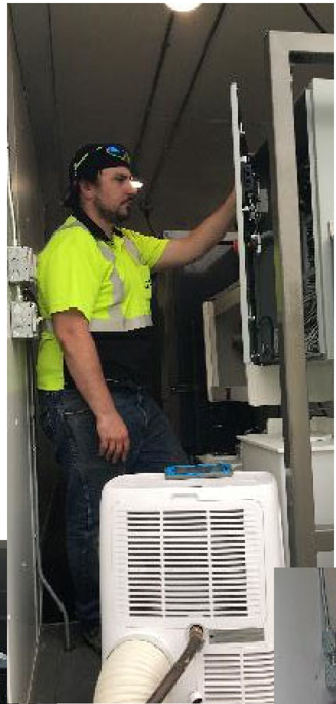

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