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Treatment of Heavy Metals and Elimination of Sulfur with a Novel Sulfate Reducing Permeable Reactive Barrier Containing ZVI

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U.S. Department of Health and Human Services
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Elimination of Heavy Metals and Sulfur with Zero Valent Iron as an Electron Donor for Sulfate-Reduction

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Acid Mine or Acid Rock Drainage

acid

H^+

heavy metals

Cu^{2+}

sulfates

SO_4^{2-}

iron

Fe^{2+}

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Acid Rock Drainage with Copper

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Stratergy: Sulfate Reduction for Acid Drainage

- Reactions of Sulfate Reducing Bacteria
  - **Increase pH:** a strong acid (sulfuric) is transformed into a weak acid (hydrogen sulfide)
  - **Reactivity:** sulfide for the precipitation of metals

- Promote Activity of the Sulfate Reducing Bacteria

  - **Provide substrate** that degrades slowly for the filling of the reactive barriers

    e.g. sawdust, compost, straw

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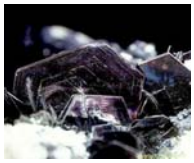
How do Sulfate Reducing Bacteria Precipitate Metals?

- Biomineralization

SO_4^{2-} + organics $\xrightarrow{biotic}$ HS^- + CO_2

HS^- $\xrightarrow{dissociation}$ H^+ + S^{2-}

$M^{2+}_{[aq]}$ + S^{2-} $\xrightarrow{abiotic}$ $MS_{[s]}\downarrow$



K_{sp} = 10^{-24} to 10^{-53}

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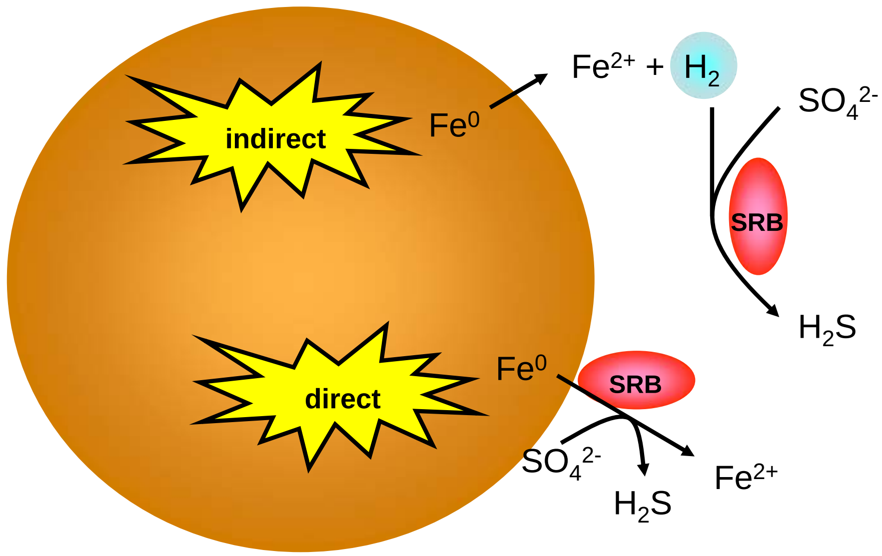
Fe^0 as an Electron Donor for Sulfate Reduction



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Fe^0 as an Electron Donor for Sulfate Reduction

indirect

- Reaction of Fe^0 (Anoxic Corrosion)

$8H^+ + 4Fe^0 \rightarrow 4H_2 + 4Fe^{2+}$ $\Delta G^{\circ\prime} = -20.1$ kJ/4 mol Fe^0

- Reaction of Autotrophic Sulfate Reduction

$2H^+ + 4H_2 + SO_4^{2-} \rightarrow H_2S + 4H_2O$ $\Delta G^{\circ\prime} = -152.2$ kJ/mol SO_4^{2-}

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Hypotheses: Benefits of Fe^0 for Sulfate Reducing PRB

- Fe^{2+} formed attenuates excess sulfides
  - → SO_4^{2-} reduced and removed, no discharge of sulfides
  - → FeS higher Ksp than heavy metal sulfides (Fe^{2+} doesn't outcompete with precipitation of heavy metals)
- Oxidation of Fe^0 forms high levels of alkalinity
  - → Can treat very acid drainage
  - → Additional metal removal mechanisms with hydroxides
- Long term source of electron donating equivalents

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Hypotheses: Benefits of Fe^0 for Sulfate Reducing PRB (*continued*)

- Direct abiotic reduction heavy metals by Fe^0

  $Fe^0 + Cu^{2+} \xrightarrow{abiotic} Fe^{2+} + Cu^0$

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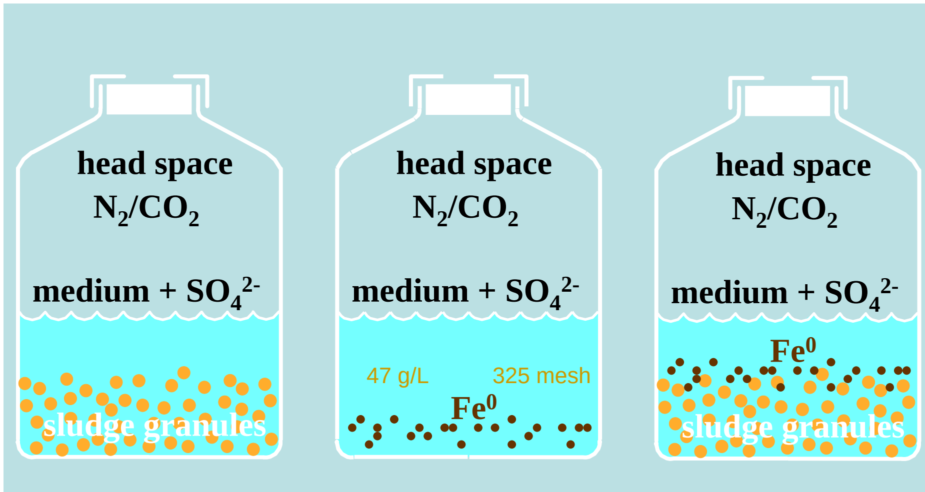
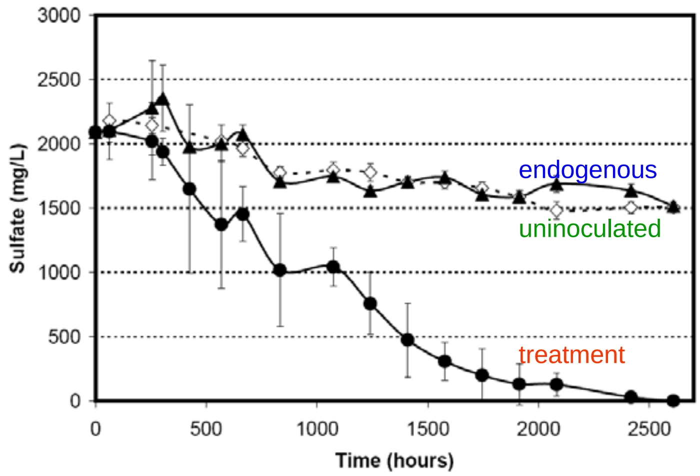
Batch Experiment: Fe^0 as E-donor SRB



endogenous control | uninoculated control | treatment

Batch Experiment: Fe^0 as E-donor SRB



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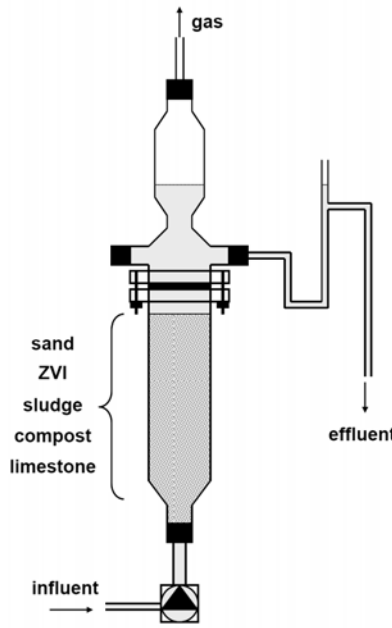
Continuous Column Experiments



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Continuous Column 1st Experiments

- Laboratory Scale PRB Columns (0.41 L)
  - **R1** Filling: Sand = 300 ml (495 g)
    Control Reactor (SO_4^{2-})
  - **R2, R3** Filling: Sand = 200 ml (331 g)
    Fe^0 = 100 ml (281 g)

    R2: Methanogenic Reactor (no SO_4^{2-})

    R3: Sulfate Reducing Reactor (SO_4^{2-})
  - **Inoculum:** SR Biofilm = 53 ml (6 g VSS)

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Continuous Column 1st Experiments

- Column Set Up
  - **Inoculum**: Sulfate reducing granular sludge from Twaron Reactor (The Netherlands)
  - **Medium**: basal inorganic nutrients
  - **Sulfate**: 1000 mg/L SO_4^{2-} for R1 & R3; 0 mg/L R2
  - **pH:** variable 7.2 to 2.5
  - **HRT:** 24 h

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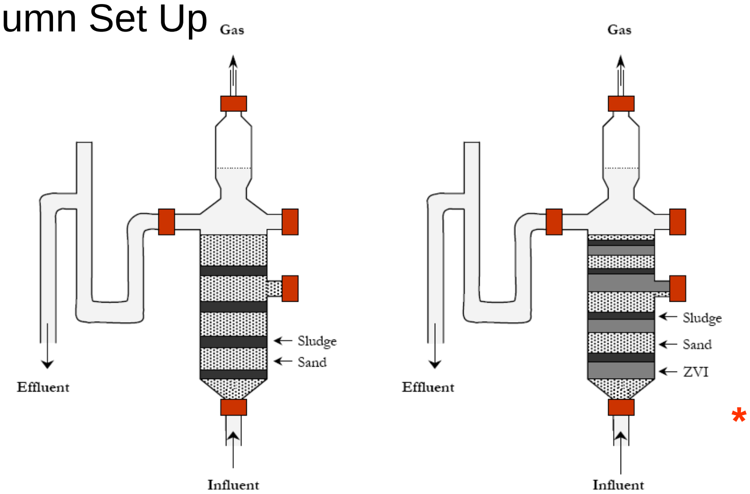
Continuous Column 1st Experiments

- Column Set Up



R1 (SO_4^{2-}) **R2** (no SO_4^{2-}), **R3** (SO_4^{2-}),

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Continuous Column 1st Experiments

Periods

I	No Metals
II	10 ppm Cu
III	25 ppm Cu
IV	50 ppm Cu
V	50 ppm Cu + 7.5 ppm Ni & Zn

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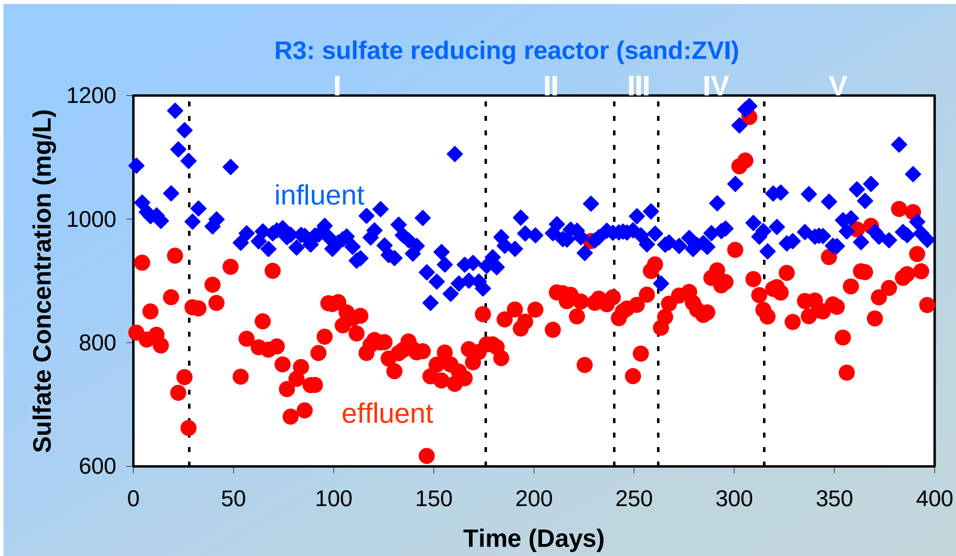
Results R3: Sulfate Data



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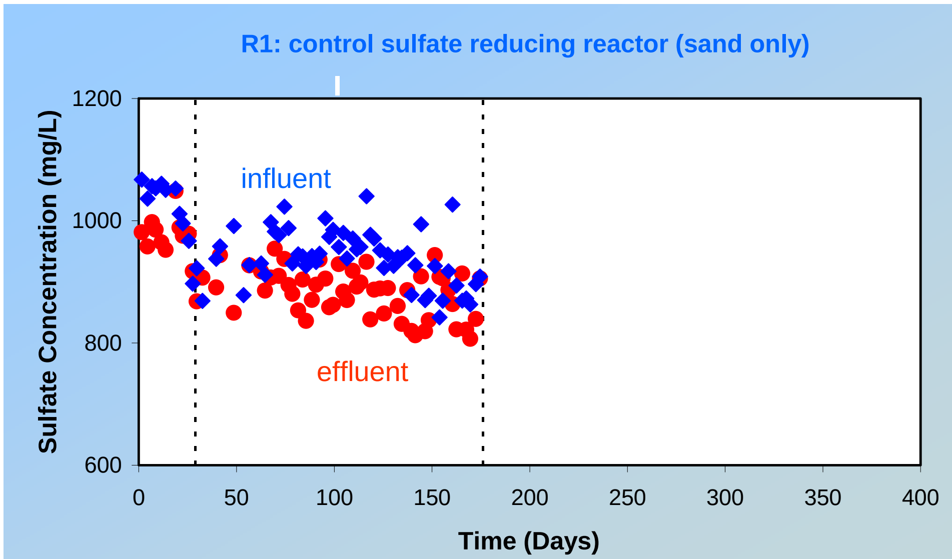
Results R1: Sulfate Data



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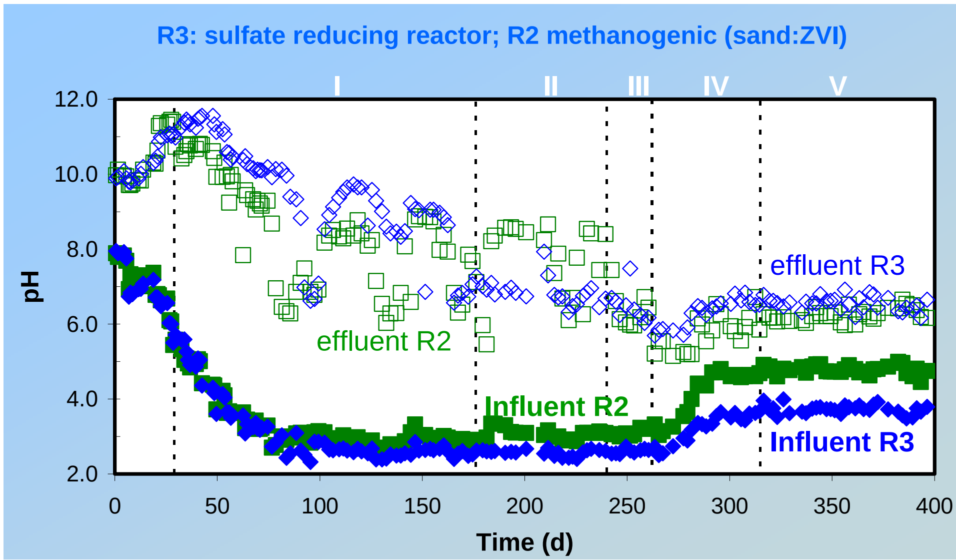
Results R2 & R3: pH



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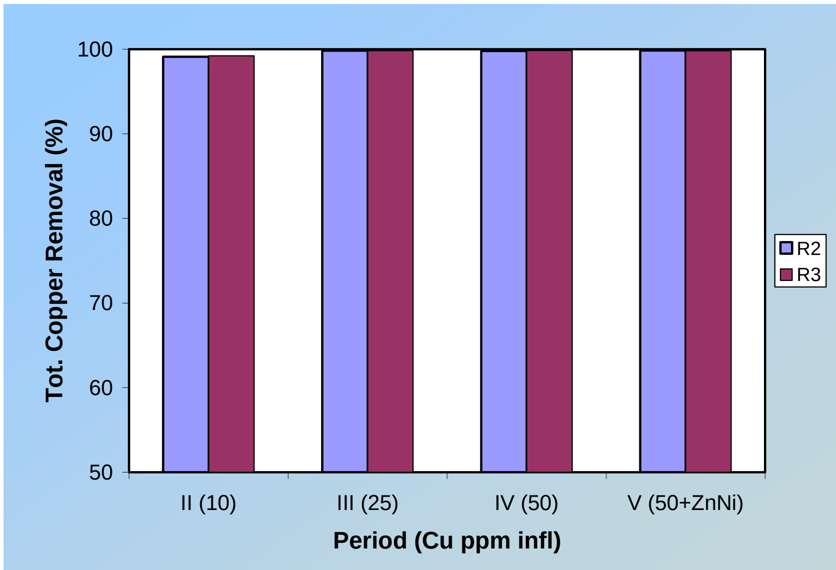
Results R2 & R3: Copper Data



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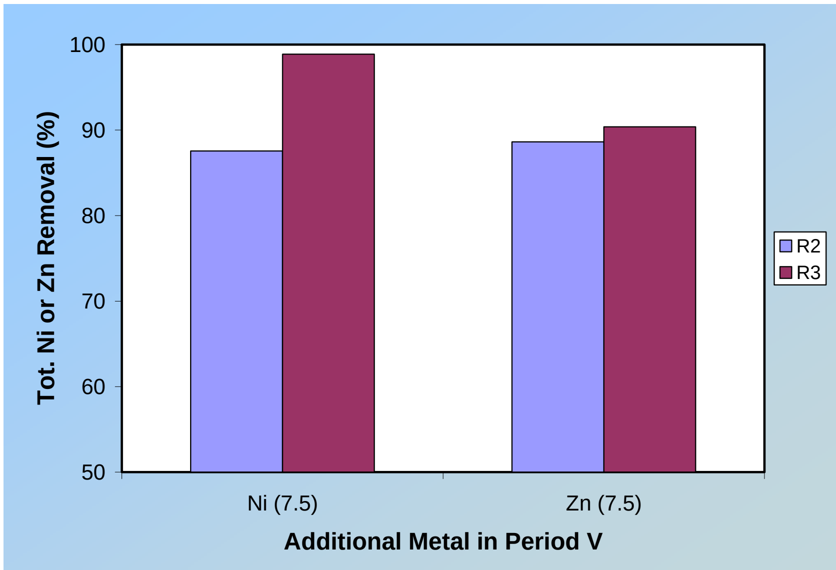
Results R2 & R3: Ni & Zn Data



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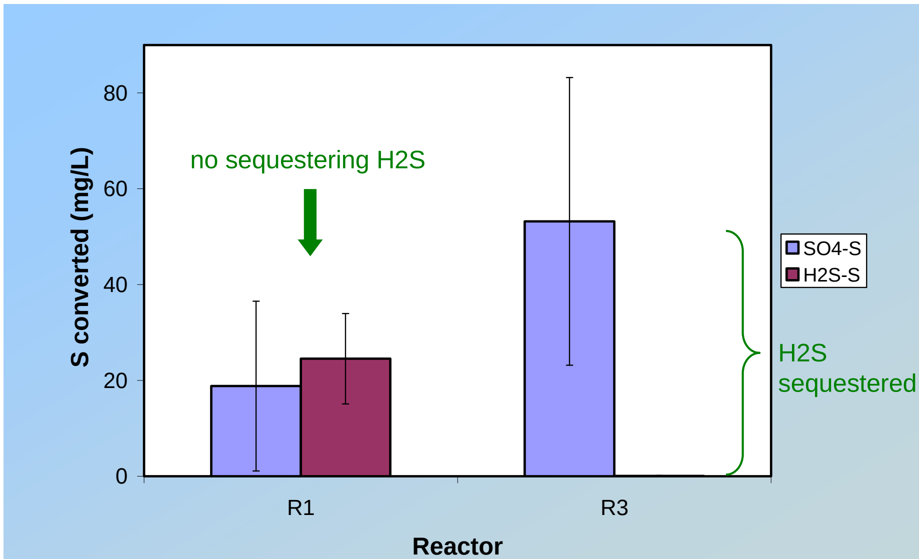
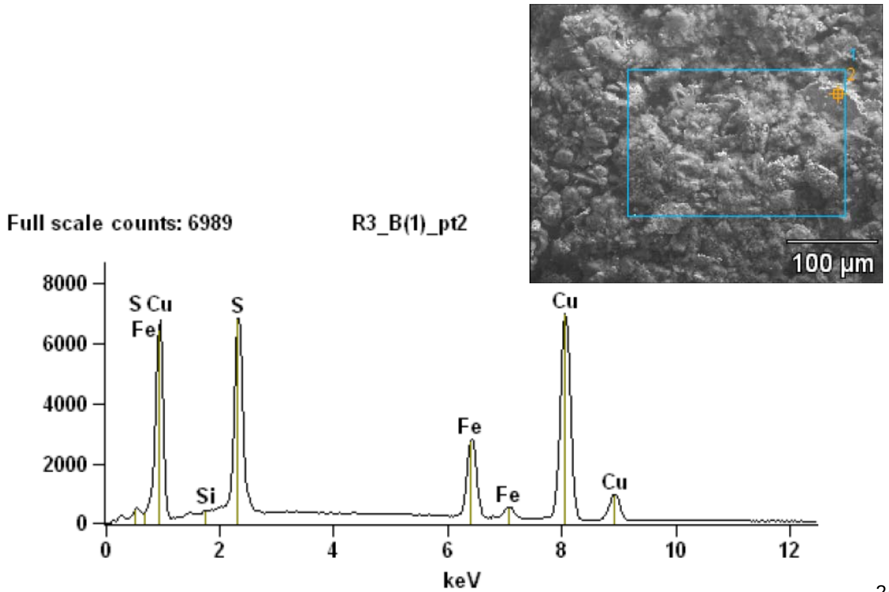
Results R1 & R3: S-Balance (day 29-175)



Results R3: SEMS-EDS



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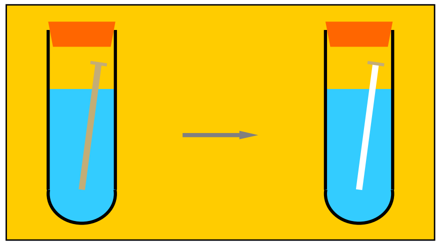
Results R2 & R3: MPN SRB

- Most Probable Number: Sulfate Reducing Bacteria

Nail in test tube method



Reactor	cells/ g dwt fill
R2 methanogenic PRB	1.0×10^2
R3 sulfate reducing PRB	1.2×10^4

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Continuous Column 2nd Experiments

- Laboratory Scale PRB Columns (0.41 L)

R4 Filling:	Compost =	210 ml (135 g)
Compost Reactor	Sand =	125 ml (191 g)
	Limestone =	18 ml (26 g)
R5 Filling:	Compost =	210 ml (135 g)
Compost-ZVI Reactor	Sand =	55 ml (82 g)
	Fe^0 =	70 ml (181 g)
	Limestone =	18 ml (26 g)
Inoculum:	SR Biofilm =	53 ml (6 g VSS)

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Continuous Column 2nd Experiments

- Column Set Up
  - **Inoculum**: Sulfidogenic granular sludge from Twaron Reactor (The Netherlands)
  - **Medium**: basal inorganic nutrients
  - **Sulfate**: initially 1000 mg/L SO_4^{2-} (50 days); remainder operation 250 mg/L SO_4^{2-}
  - **pH:** variable 7.2 to 3.0
  - **HRT:** 24 h
  - **Cu: Period** A = 10, B = 25, C = 50, D = 20 ppm

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R4

R5

Cu^0

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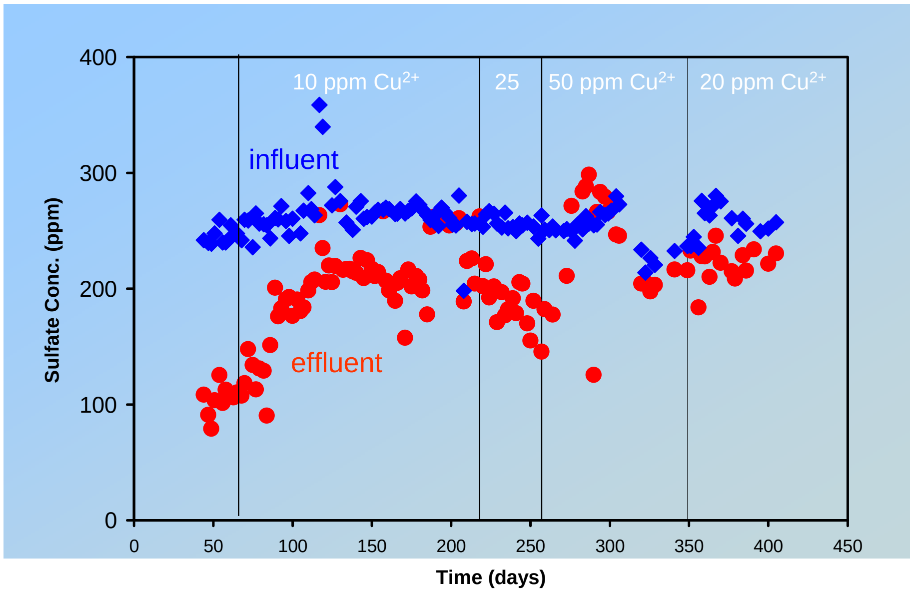
Results R4: Sulfate Data



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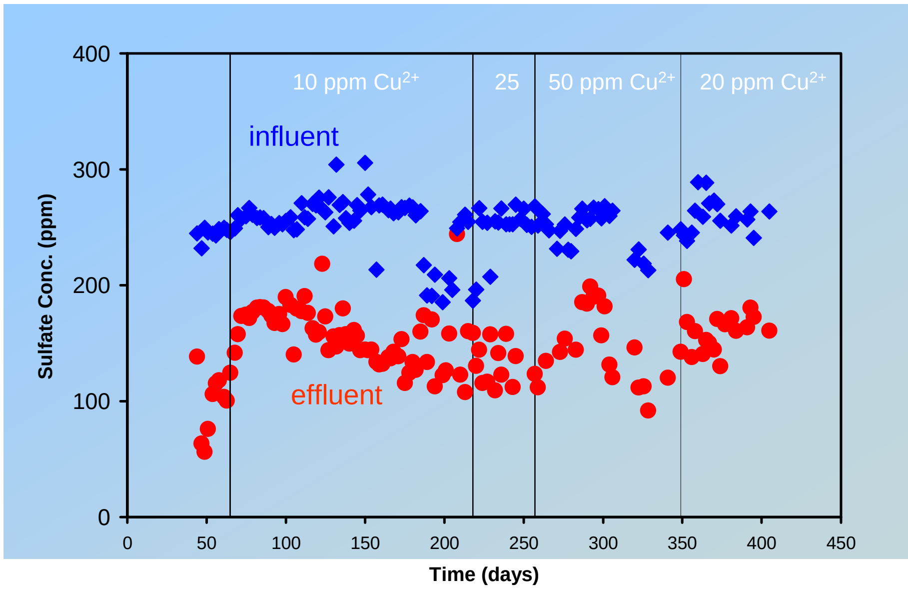
Results R5: Sulfate Data



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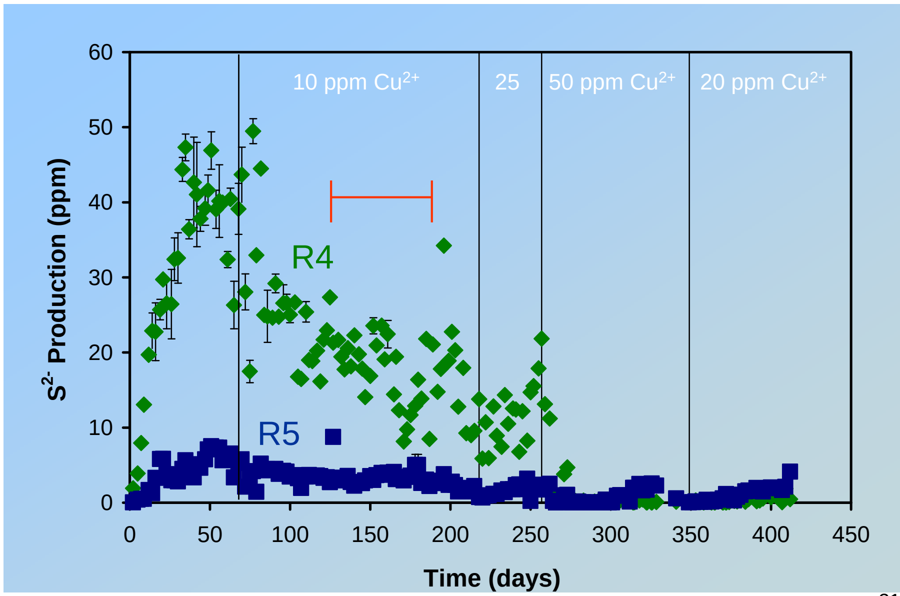
Results: Sulfide Data



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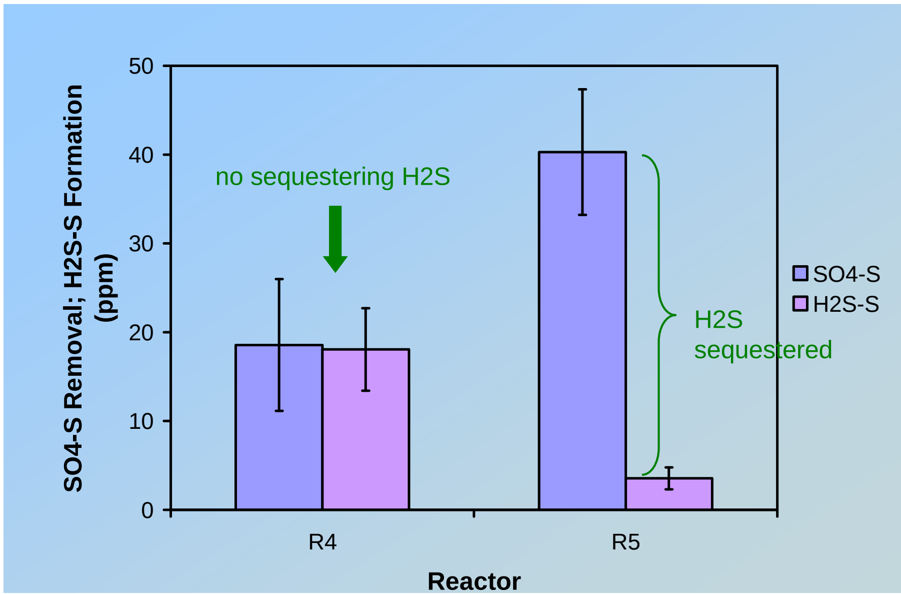
Results: S Balance (days 125-185)



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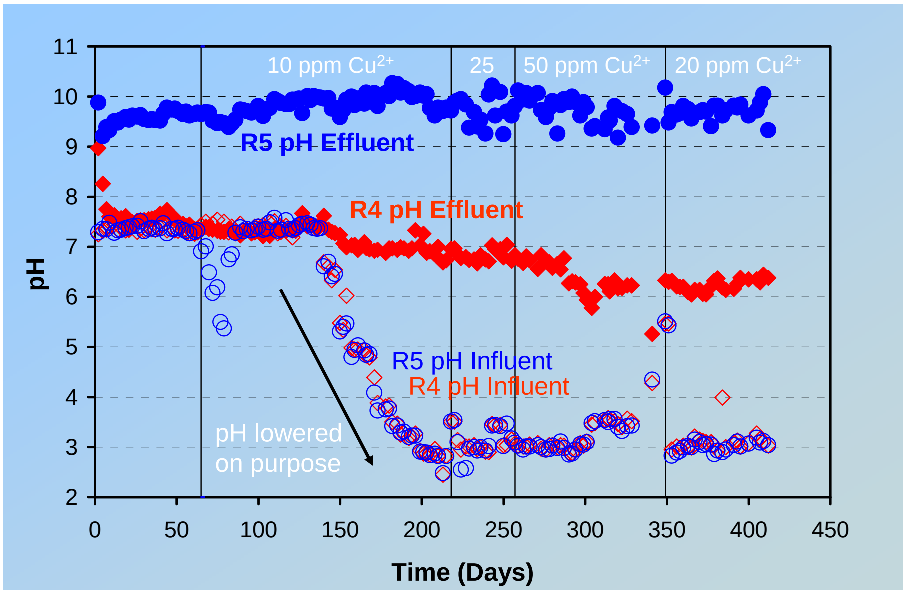
Results: pH



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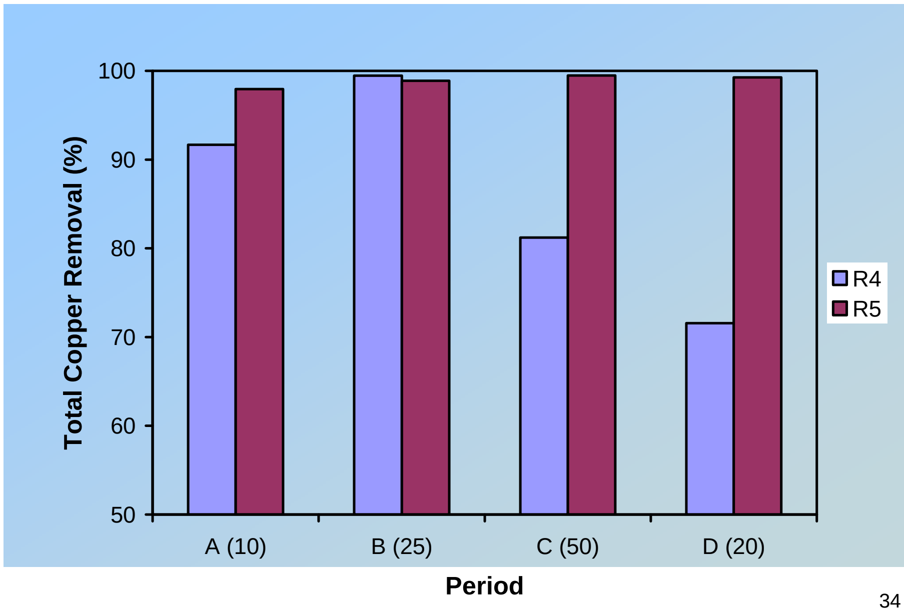
Results: Total Cu Removal (%)



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Continuous Column 3rd Experiments

- Laboratory Scale PRB Columns (1.3 L)
  - **R6** Filling:
    Compost-ZVI Reactor

Compost =	526 ml (78 g)
Sawdust =	272 ml (24 g)
ZVI =	14 ml (36 g)
Limestone =	45 ml (73 g)

HRT: 48 h

$\mathbf{SO_4^{2-}}$: 250 mg/L

Cu: 10, 30, 75, 150, 300, 75 ppm

  - **Inoculum:** Mix Biofilm = 108 ml (14 g)

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Continuous Column 3rd Experiments

- Limestone Reactor, Pretreatment Column (0.7 L)
  - **LR** Filling: Limestone = 623 ml
  - **HRT**: 24 h

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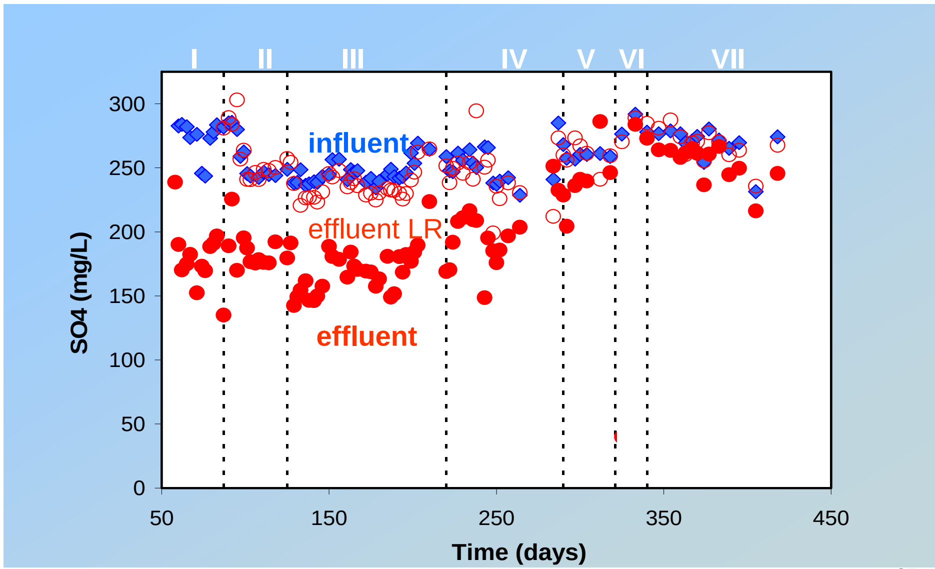
Results R6: Sulfate Data



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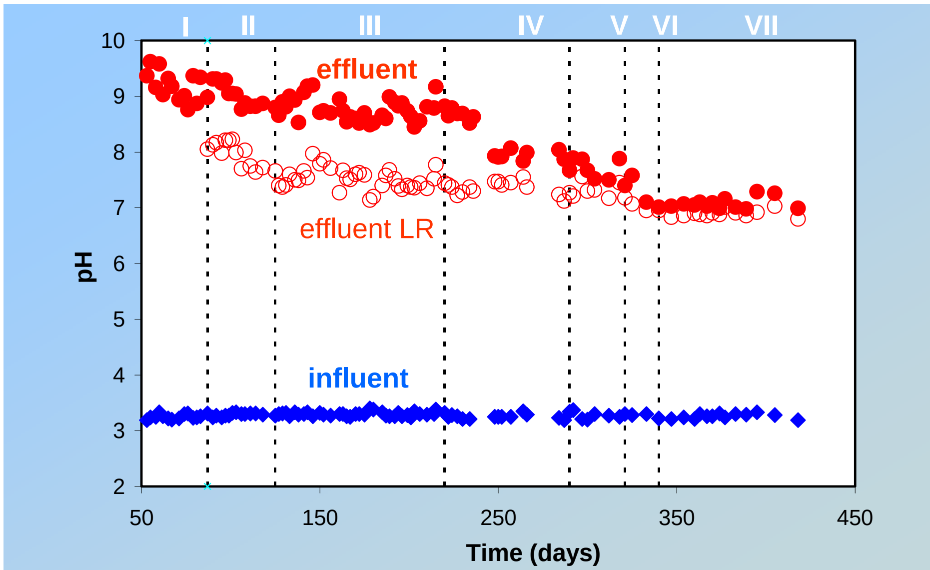
Results R6: pH Data



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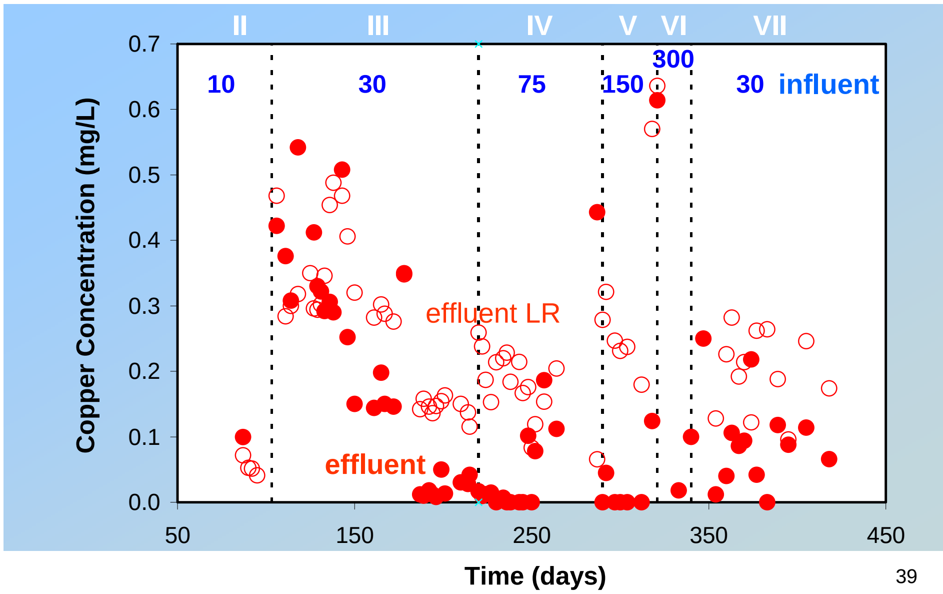
Results R6: Soluble Cu Data



Summary Chart

Average performance from day 175 to day 240

Reactor	ZVI	Comp	LS	Sand	SO_4^{2-}	pH incr.	Cu rem.
	% dwt				mg/L_r.d		%
R3	46	0	0	54	33	4.3	99.8
R4	0	38	7	53	29£	3.8	99.0£
R5	42	31	6	19	76	6.8	99.7
R6*	16	45†	32	0	33	5.4*	99.9*

*preceded by limestone reactor — efficiency post treatment polishing in PRB (89.5)

†includes sawdust

£decreased when compost biodegradability was exhausted after day 270

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Conclusions

- Compost and the mixture of compost/Fe^0 are good substrates for sulfate reducing bacteria
  - Elimination of Total Copper: 99.5%
  - Drops in R4 to 72% when SO_4^{2-} reduction ceased (exhaustion of compost biodegradability)
- Fe^0 increases the removal of sulfate
  - Prolonged supply of electron equivalents
- Fe^0 prevents the discharge of excess sulfur
- Fe^0 increases the alkalinity

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