Evaluation of Reactive Cap Amendments to Sequester Dissolved Manganese in Upwelling Groundwater

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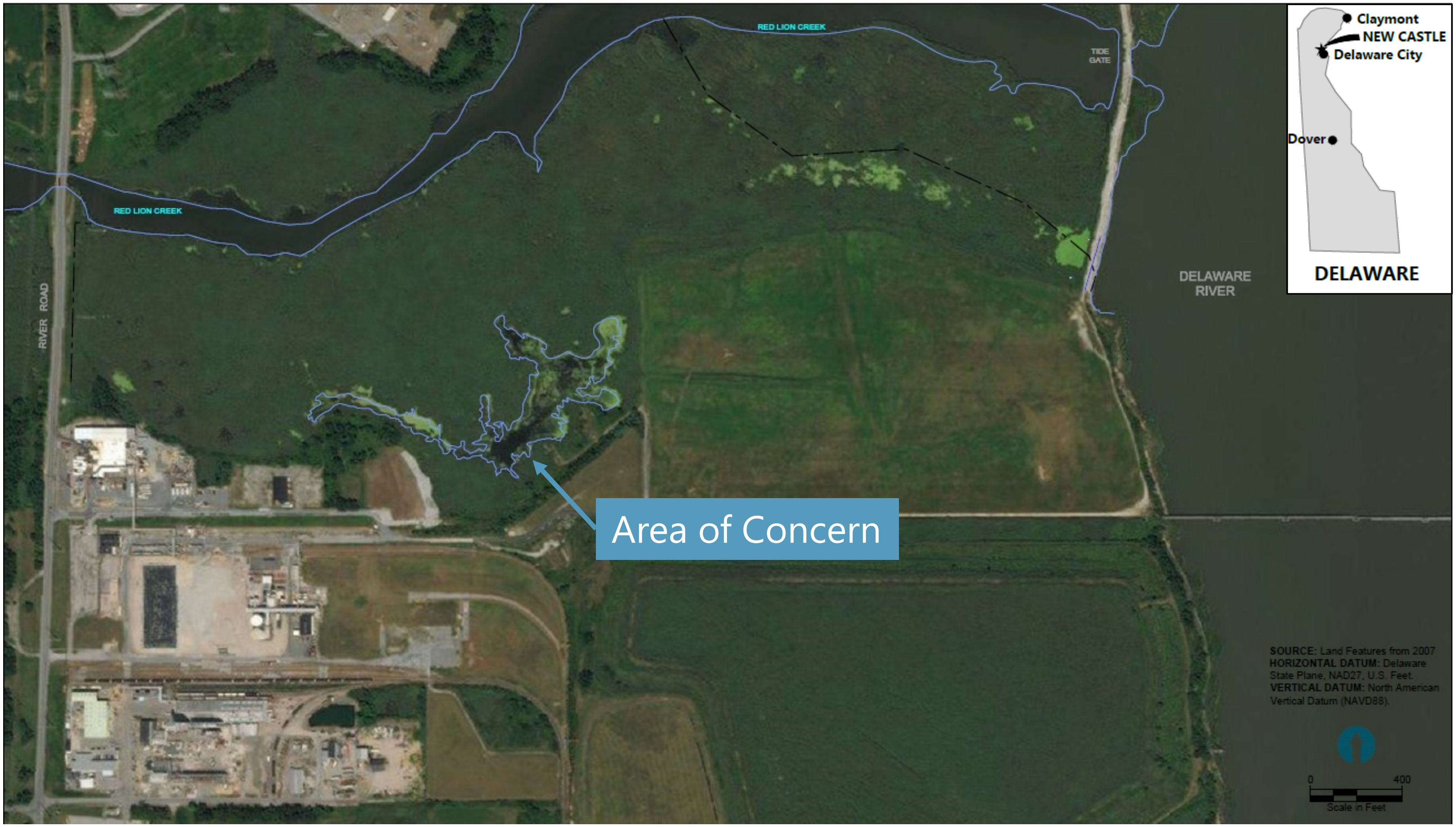
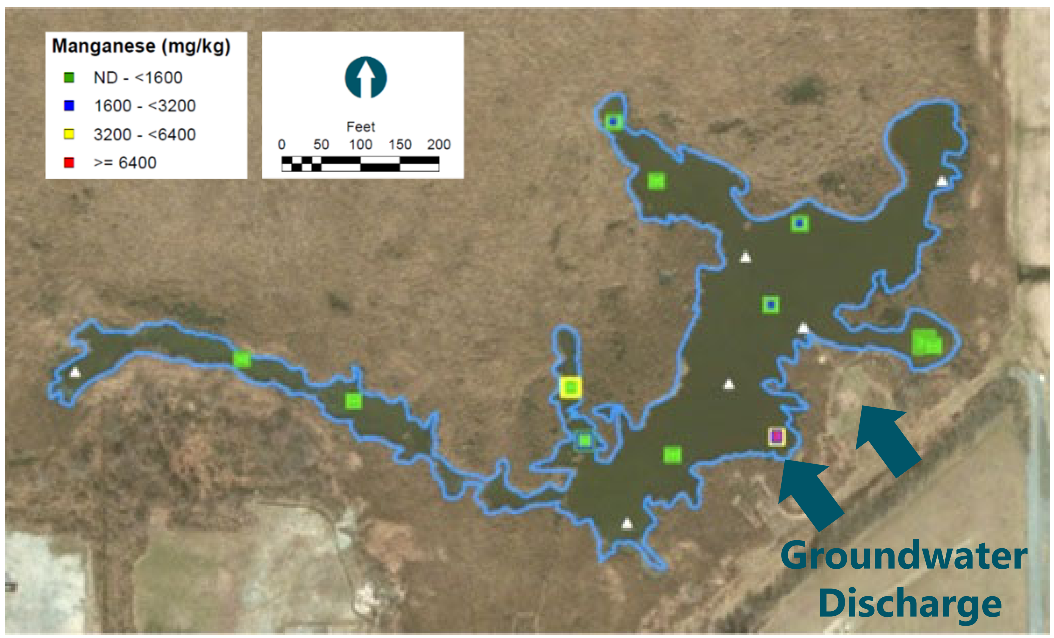
Site Overview

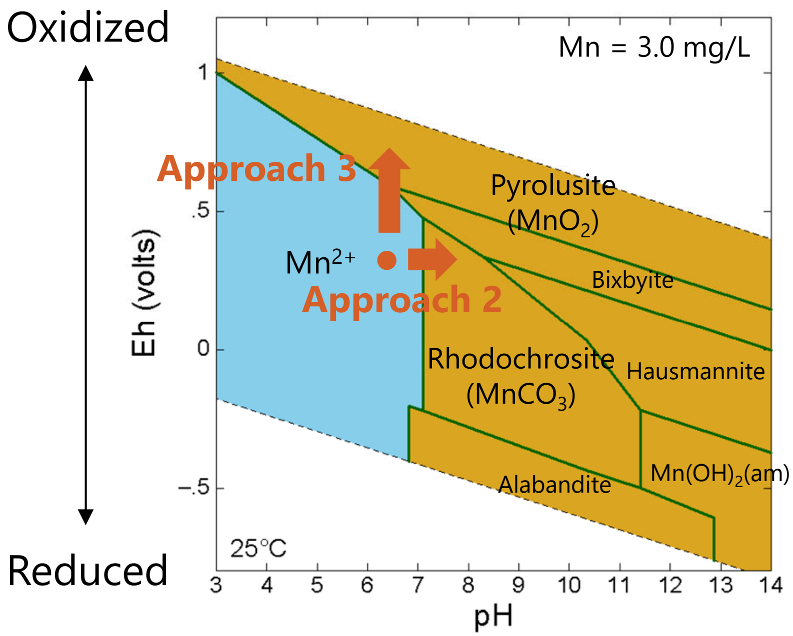


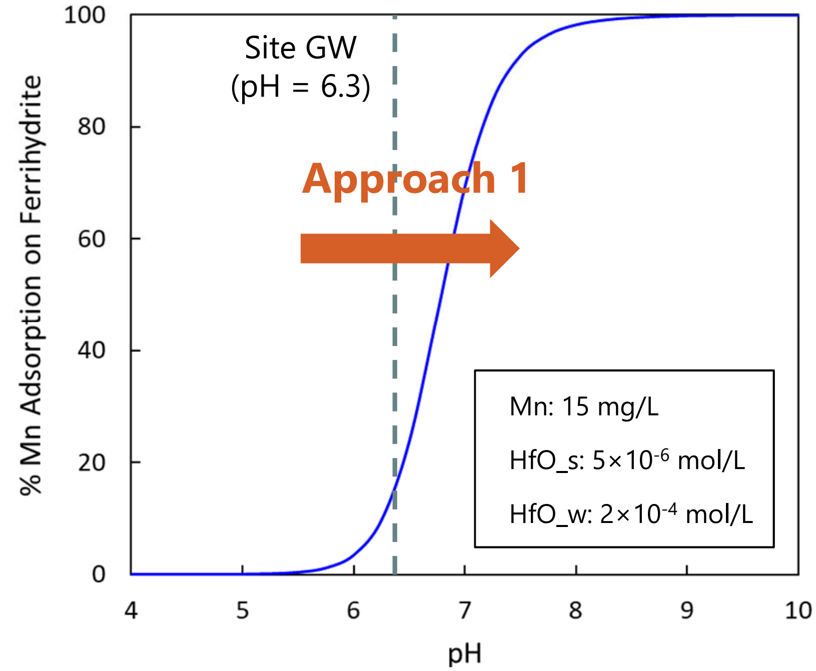
Background

- Former chlor-alkali facility (1964 to 2005) currently undergoing remediation
- Dissolved manganese (Mn) groundwater plume and elevated Mn concentrations detected in sediments and surface water in an area of groundwater discharge



Manganese (Mn) Geochemistry





- Dissolved Mn(II) is thermodynamically stable in the site groundwater
- Approaches for Mn(II) removal
  1. Adsorption on iron oxides by increasing pH
  2. Precipitation of manganese carbonate (rhodochrosite) by increasing pH
  3. Oxidation and precipitation of manganese oxides under aerobic conditions

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Objectives

1. To evaluate and select a reactive cap amendment for Mn removal from upwelling groundwater to protect sediment and surface water quality at the site

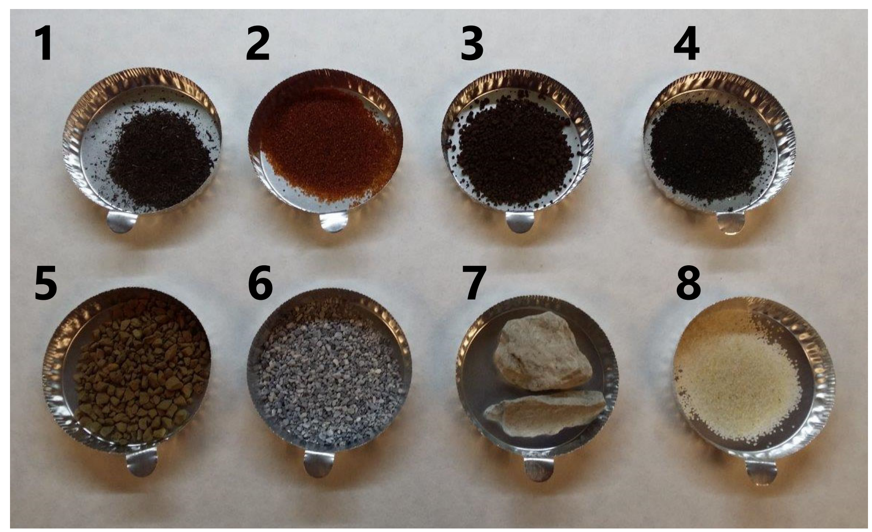
2. To assess Mn removal efficiency and capacity of reactive media and long-term stability of sequestered Mn

Batch Tests

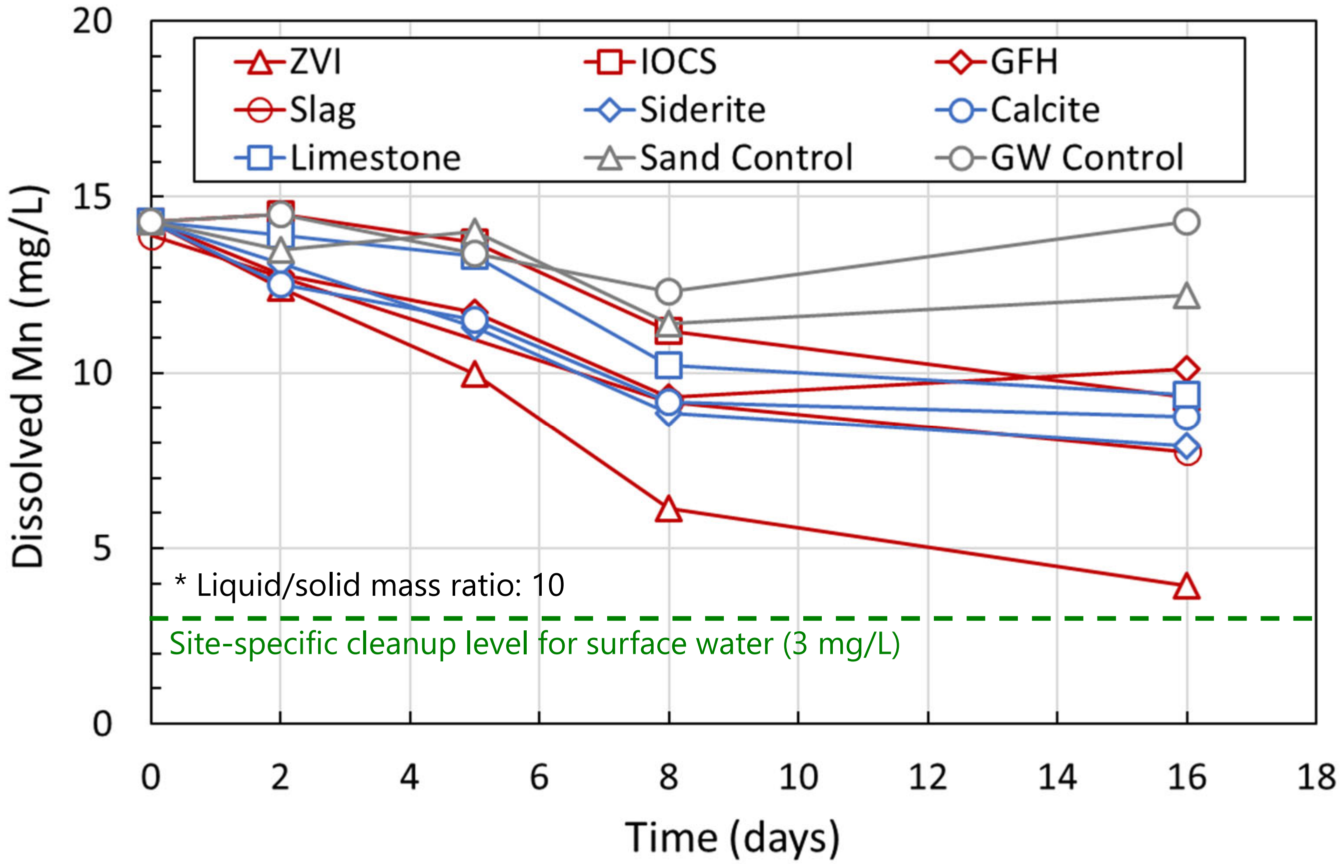
- 8 different reactive amendments tested (single or mixed)
- Liquid/solid mass ratio: 2, 5, and 10
- Site groundwater from three different wells with a range of dissolved Mn (5.8, 14.3, and 25.1 mg/L)
- Reacted in batch reactors up to 16 days under nitrogen atmosphere

Reactive Media Tested

1. Zero-valent iron (ZVI)
2. Iron-oxide coated sand (IOCS)
3. Granular Ferric Hydroxide (GFH)
4. Iron-Oxide Slag
5. Siderite ($FeCO_3$)
6. Calcite ($CaCO_3$)
7. Crushed limestone
8. Sand (as control)

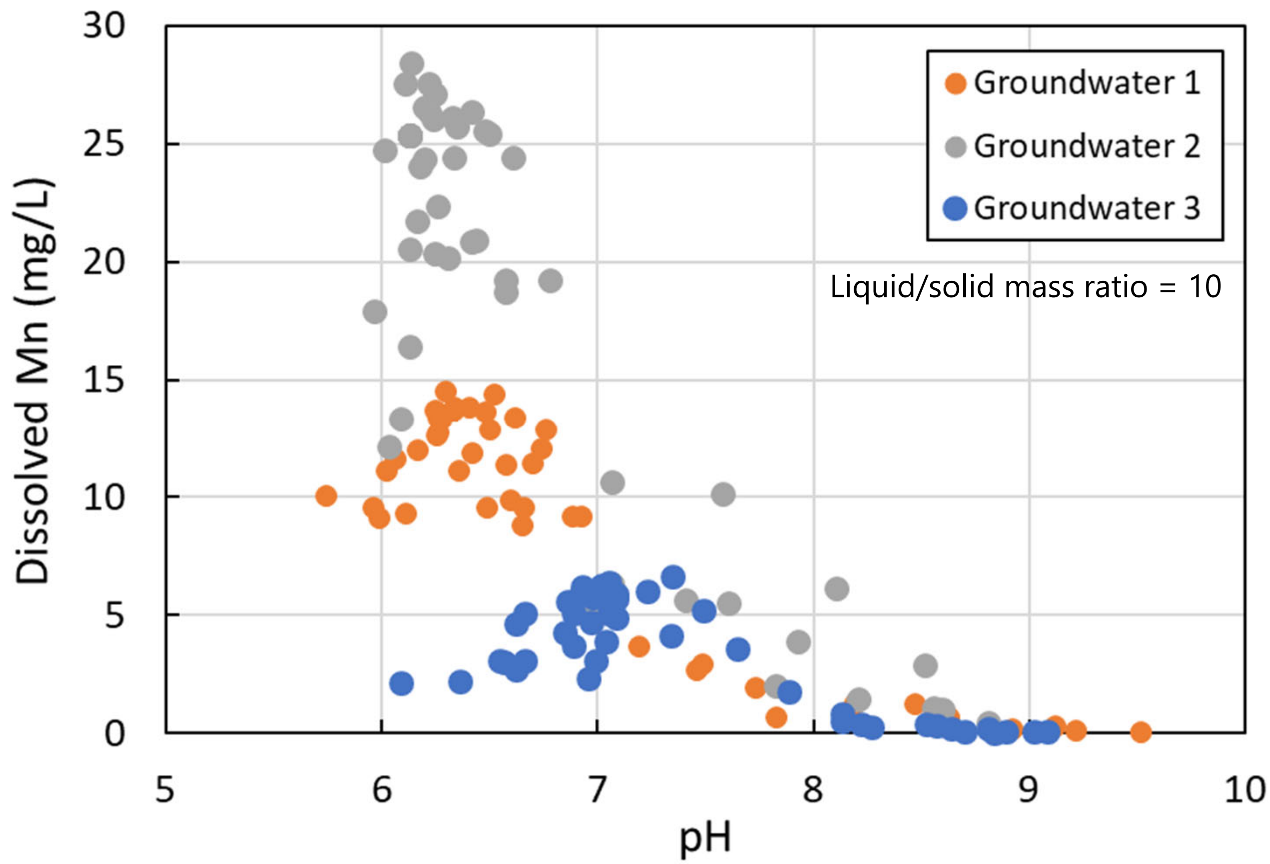


Batch Test Results



ZVI had highest Mn removal efficiency, but the reaction rate was slow and correlated with pH increase due to ZVI corrosion reactions

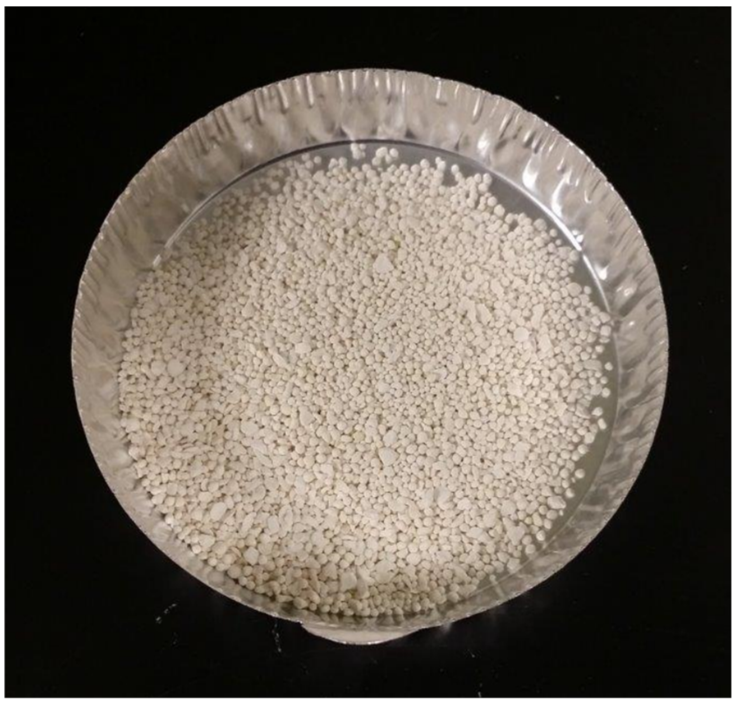
pH Effect on Mn Removal in the Batch Tests



Increasing pH is important to enhance Mn removal by the reactive amendments

Magnesium Oxide (MgO)

- MgO hydrates to $Mg(OH)_2$ and buffers pH at approximately 10.7
- Additive to enhance Mn removal



$$MgO + H_2O \rightarrow Mg(OH)_2$$

$$Mg(OH)_2 \rightarrow Mg^{2+} + 2OH^-$$

buffers pH

Flow-Through Column Tests

- 4 different mixtures of reactive amendments with sand were tested
- Influent solution: site groundwater (Mn concentration: approximately 15 mg/L)
- Performed for approximately 40 days

Column 1

ZVI: 25

Calcite: 25

Sand: 50

Column 2

ZVI: 25

Slag: 25

Sand: 50

Column 3

Slag: 47.5

MgO: 2.5

Sand: 50

Column 4

Calcite: 47.5

MgO: 2.5

Sand: 50

Note: measurements in wt%

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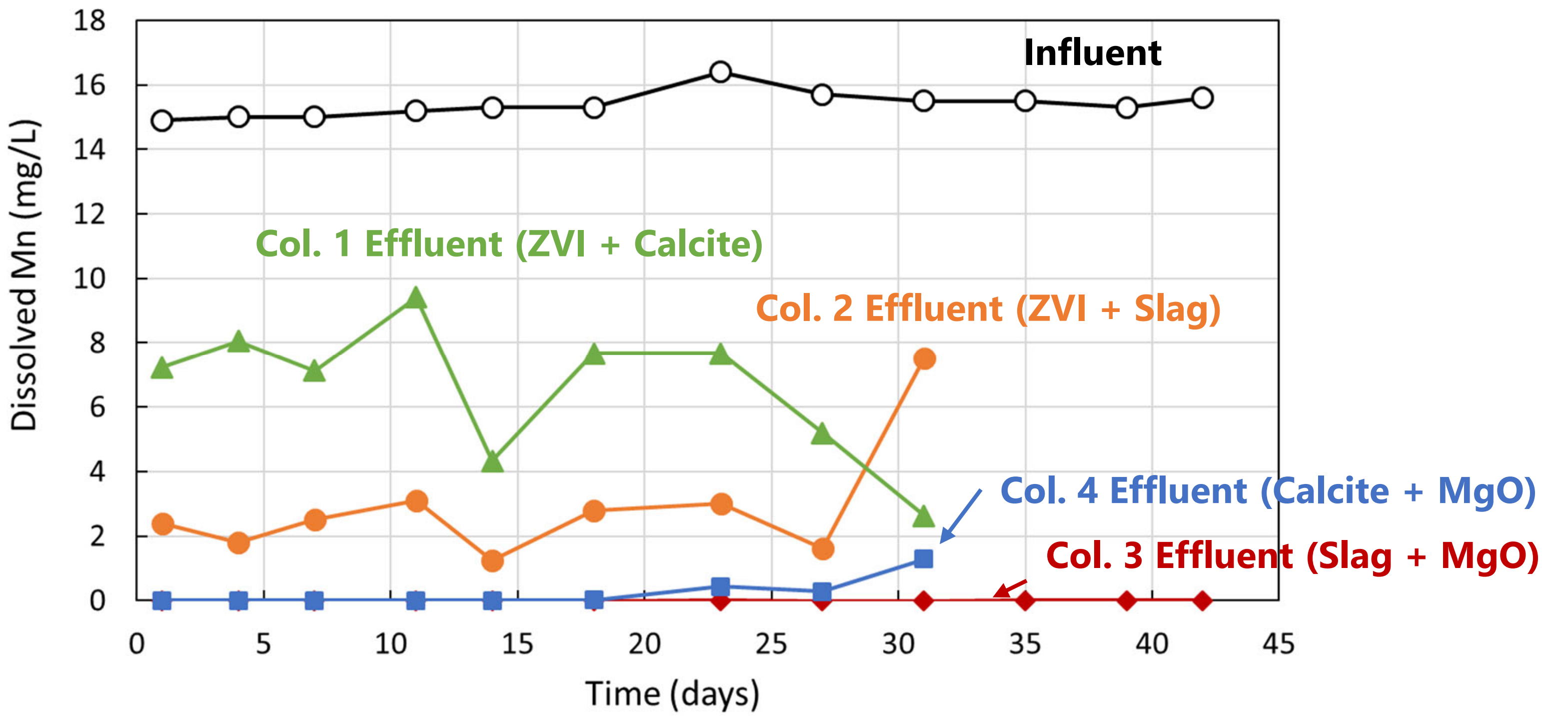
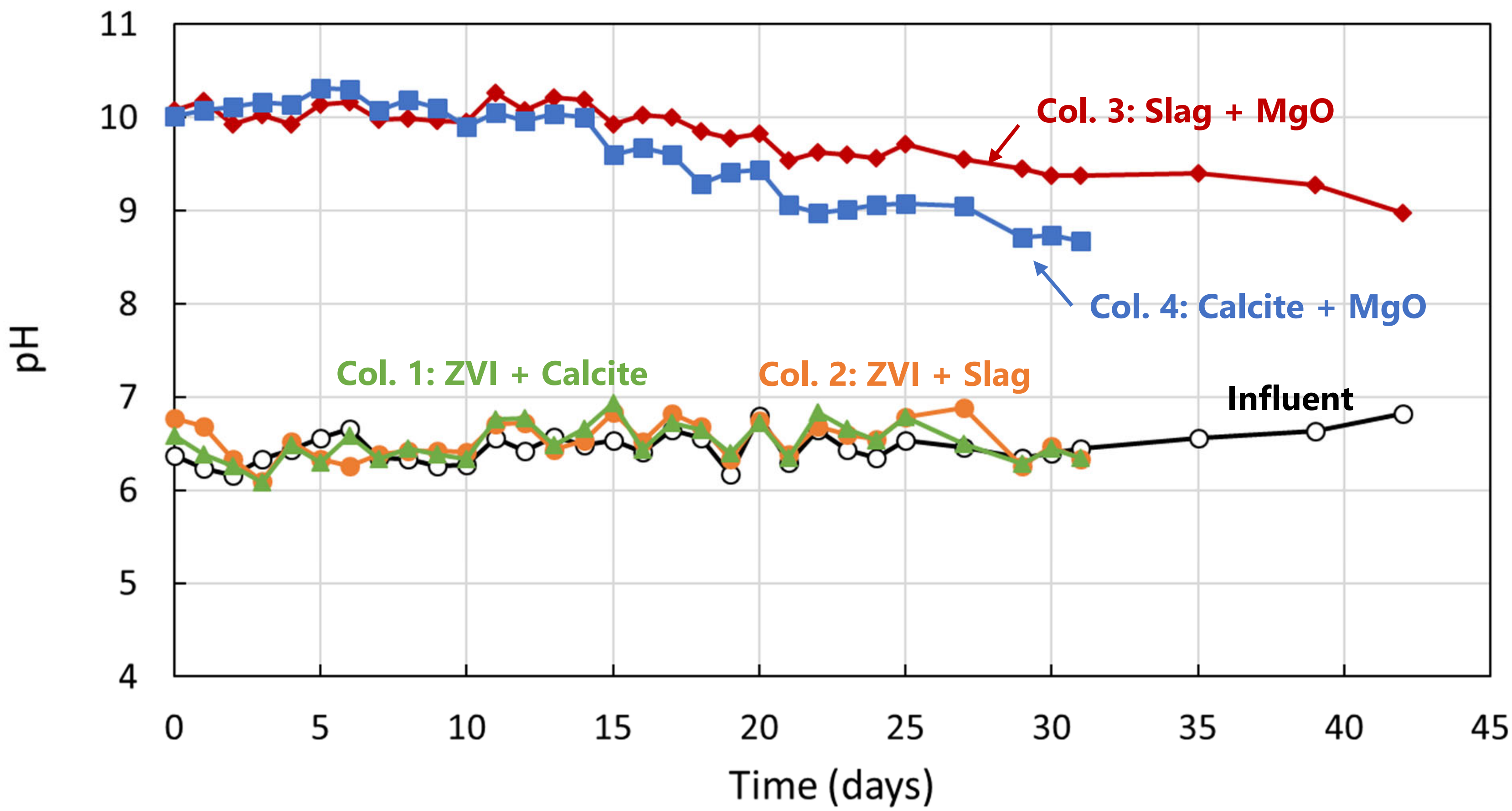
Flow-Through Column Test Setup

Column Test Results



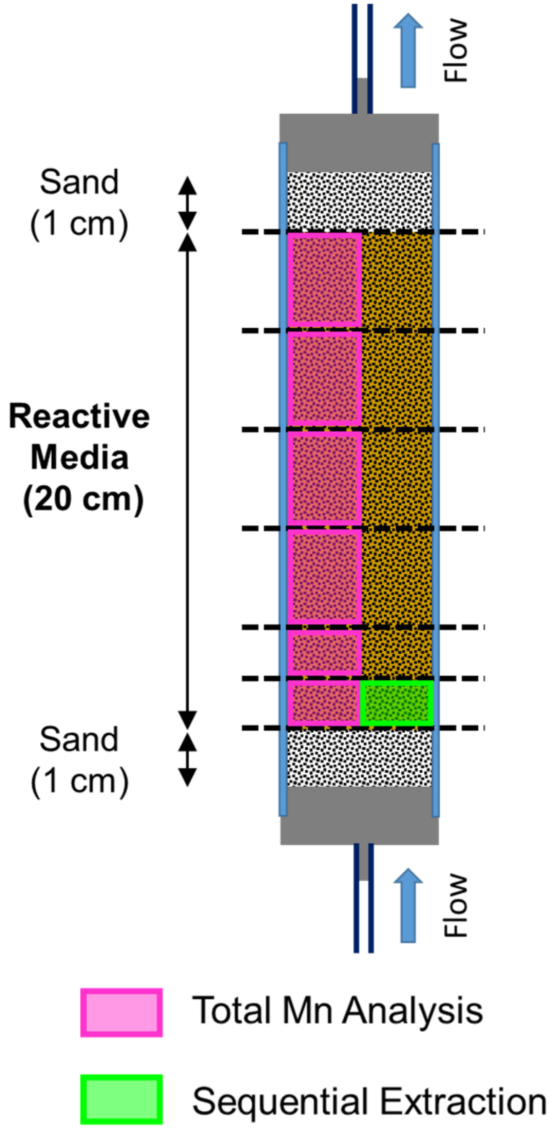
- Column 3 (Slag + MgO) and Column 4 (Calcite + MgO) were more effective to remove Mn from site groundwater
- Maintaining pH above 7 is critical for enhancing Mn removal

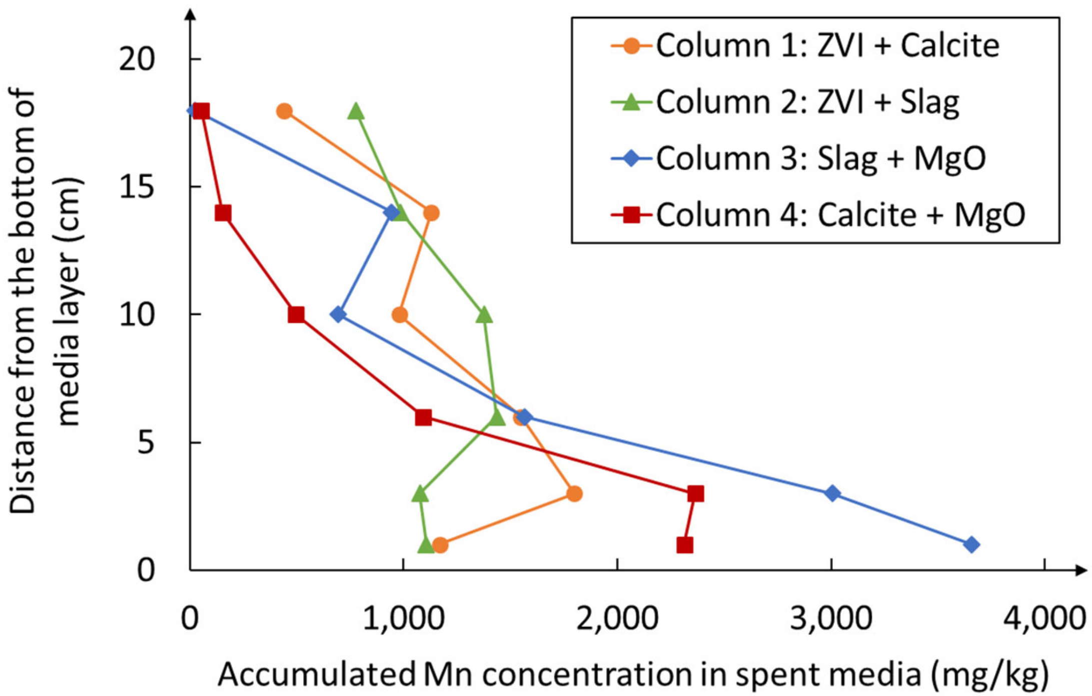
Column Test Results (cont.)



- MgO maintained pH above 7 in effluents from columns 3 and 4

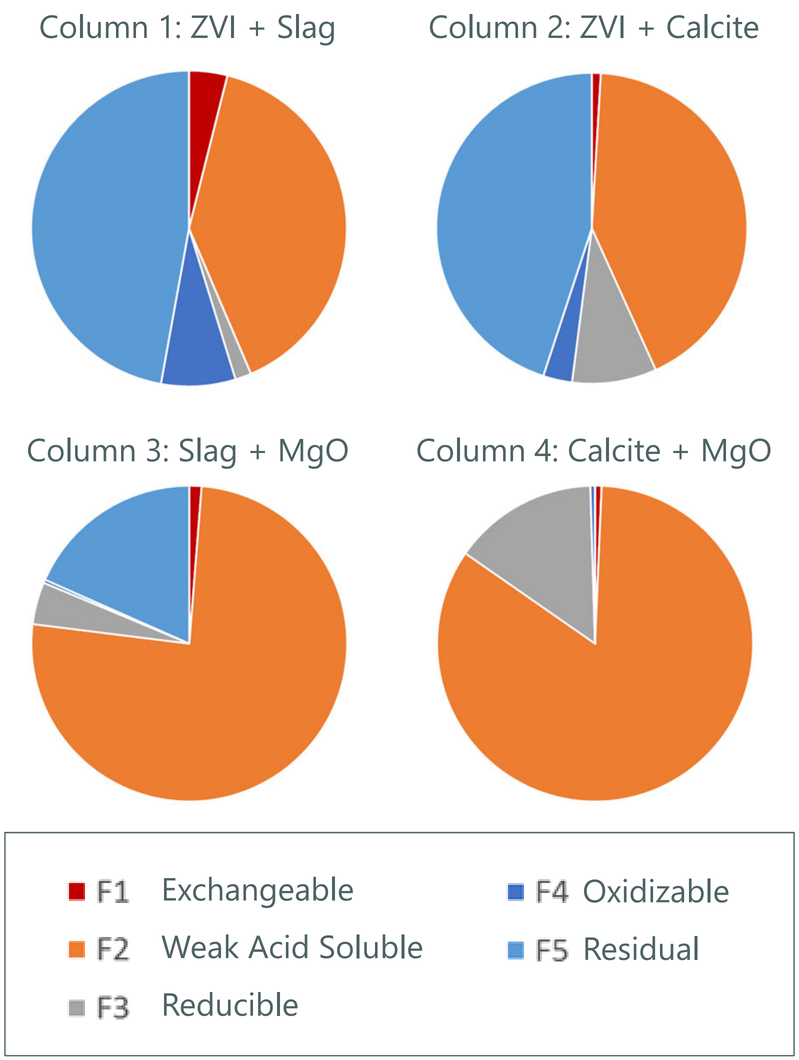
Accumulated Mn in Column Media





Sequential Extraction of Spent Media

- Fractions arranged in order of increasing sequestration strength in solid phases
- Most Mn taken up by media is in F2, reflecting Mn bound to oxides and/or carbonates
- In both ZVI columns and Slag + MgO, Mn uptake in F5 (residual, very strongly sequestered) is also important (likely due to aging of Mn-bearing Fe oxide phases to more stable forms over time)



Conclusions

- Addition of MgO enhanced Mn removal efficiency and capacity by iron-oxide slag and calcite
- The enhanced Mn removal by MgO was attributed to its pH buffering capacity (9-10)
- Duration of column tests scales to approximately 3.5 years in field (approximately 5 years for Slag + MgO without breakthrough)
  - Solid phase Mn profiles provide estimate of media capacity
  - Data can be used to iterate cap design for 100-year cap life

Questions/Discussion