Geochemical Modeling to Assess Impacts of Chat Fine Injections on Aquifer Quality at the Tar Creek Superfund Site, Oklahoma

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Study Region
Legacy of Tri-State Lead-Zinc Mining
Study Objectives

• Reduce dust hazard by removing chat piles
• Separate coarse chat (usable for road base) from fine chat
• Inject fine chat slurry into mine rooms below piles
• Conduct long-term pilot study to assess feasibility and monitor water quality
• Sooner Pile chosen as test area
• Use geochemical modeling to
  – Verify observed results
  – Predict long term effects on water quality
Chat Size Fraction Separator ("Sandscrew")
Chat Size Fraction Separator ("Sandscrew")
Injection of Fines Slurry
Geochemistry and Transport Modeling
Geochemical Signatures

• Boone Aquifer
  – Mineralized zones: Ca-SO₄, high TDS, trace metals
  – Non-mineralized: variable chem, low TDS, low trace metals

• Mine Pool Water
  – Ca-SO₄, Higher TDS than Boone, trace metals

• Rubidoux
  – Ca/Mg-HCO₃/SO₄, low TDS, very low trace metals
TDS vs. pH

Boone Chat Pile Mine Pool Rubidoux Sandscrew Discharge Tailings Pond

Total Dissolved Solids, mg/L vs. pH
Zinc vs. Bicarbonate Pct.

- Zinc, mg/L
- Bicarbonate, as percentage of anions

Locations:
- Boone
- Chat Pile
- Mine Pool
- Rubidoux
- Sandscrew Discharge
- Tailings Pond

Graph shows the relationship between Zinc concentration and Bicarbonate percentage across different locations.
Chat and Chat Fines Composition – XRD Analysis

- Bulk chat primarily comprised of chert (amorphous SiO$_2$) – over 90%
- Minor carbonates (calcite, dolomite)
- Trace sulfide, oxide, clay minerals
- Fine fractions shown to have higher concentrations of metals
Chat and Chat Fines
Modeled Trace Metal Minerals

• **Primary Minerals**
  – Sphalerite (ZnS); Cd associated
  – Galena (PbS)
  – Pyrite (FeS$_2$); As associated

• **Secondary Minerals**
  – Carbonates of Zn, Cd, Pb, and Fe
  – Sulfates of Pb, Fe
  – Minor silcates (hemimorphite = Zn source)
  – Oxides of Cd, Fe (plus adsorbed metals on FeO’s)
Reactions During Injection

• Chat fines mixed with mine pool water
  – Dissolves minerals in fines, releasing trace metals
  – Carbonates buffer acidity released by sulfide oxidation
  – Mixing at surface ensures oxygen presence in solution
  – Process modeled with PHREEQC
Reactions During Injection (cont’d)

• Chat fines slurry injected into mine pool
  – Oxygen-rich water mixes locally with more reduced mine pool water and iron oxides precipitate
  – Iron oxides act as co-precipitates with and adsorbents for trace metals (especially arsenic and lead)
  – Process modeled with PHREEQC
PHREEQC Model

- **Observed minerals in chat are added to Sooner Pilot Study supply water (MMB2)**
  - Zinc, lead, and cadmium sulfides
  - Calcite and dolomite
  - Resulting water reasonably resembles slurry water injected into mine pool

- **Slurry water is mixed with mine pool water in various proportions with mineral precipitation and dissolution controls**
  - Solubility controlled by sulfate and carbonate minerals
  - Result resembles injection well samples if ratio of mine pool water to slurry water is 2:1
**PHREEQC Model Results**

Dissolution of cadmium, lead, and zinc sulfides and calcium/magnesium carbonate; Precipitation of calcium, zinc, and cadmium carbonates and of iron oxide

<table>
<thead>
<tr>
<th>Description</th>
<th>Sample ID</th>
<th>Date</th>
<th>Metals in ug/L</th>
<th>Fe</th>
<th>Zn</th>
<th>Cd</th>
<th>Pb</th>
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</thead>
<tbody>
<tr>
<td>Mine pool water used to slurry fine chat</td>
<td>MMB2</td>
<td>07/17/08</td>
<td></td>
<td>391</td>
<td>25,900</td>
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<td>276</td>
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<tr>
<td>Water portion of fine chat slurry in sandscrew tank</td>
<td>SNDSCR</td>
<td>07/17/08</td>
<td></td>
<td>&lt;25</td>
<td>20,300</td>
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<td>294</td>
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<tr>
<td>PHREEQC simulation results</td>
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<td></td>
<td>&lt;25</td>
<td>20,967</td>
<td>339</td>
<td>318</td>
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</tbody>
</table>

Mix pre-injection mine pool water with SNDSCR water in the ratio 2:1; Dissolution of gypsum; Precipitation of iron oxide

<table>
<thead>
<tr>
<th>Description</th>
<th>Sample ID</th>
<th>Date</th>
<th>Metals in ug/L</th>
<th>Fe</th>
<th>Zn</th>
<th>Cd</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
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<td>Pre-injection mine pool water at Sooner Pile</td>
<td>SMB2</td>
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<td>&lt;25</td>
<td>20,300</td>
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<td>294</td>
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<td>First post-injection mine pool sample at Sooner Pile</td>
<td>SMB2</td>
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<td>&lt;25</td>
<td>14,666</td>
<td>143</td>
<td>100</td>
</tr>
</tbody>
</table>
Short-Term Pilot Studies: Lead

[Graph showing concentration in µg/L over time from 10/01/04 to 03/24/10 for RMB3, FCB3, and TMB3]
Short-Term Pilot Studies: Cadmium
Short-Term Pilot Studies: Zinc
PHAST Model

- Groundwater flow and solute transport model combined with PHREEQC
- Transport simulated with parameters from site groundwater flow model (conductivity, gradients) and modified with transport parameters
  - Dispersion
  - Cation exchange
  - Adsorption
  - Mineral precipitation
PHAST Simulations

• Pre-injection mine water introduced as continuous flow into Boone Aquifer (outside of mine influence): 40 years
• Sooner injection well data were diluted based on results from dilution simulation within mine workings: 5-year injection
• Diluted water flows into Boone: 20 years
• One-dimensional flow was simulated for simplicity
PHAST Simulations

- Post-injection water represented by October 2009 sample from well SMB3 – washed fines injection well from Sooner Pile
- General mine pool water represented by pre-injection sample from well SMB2 – also from Sooner Pile
- These two waters were mixed in different proportions using PHREEQC to represent different stages of discharge into Boone
- Boone aquifer represented by well BW13 – outside of mine influence
PHAST Model Layout: Phase 1

Pre-Injection Mine Water (Ca-SO₄, pH 6.3)

Undisturbed Boone Aquifer (Na-HCO₃, pH 8.6)

- Adsorption to Iron Oxide Surfaces
- Exchange Reactions on Carbonate and Clay Mineral Surfaces
- Precipitation of Metal Carbonate Minerals

2,000 Feet
PHAST Model Layout: Phase 2

Diluted Post-Injection Water (Ca-SO₄, pH 6.3-6.6)

Boone Aquifer Affected by Historical Mine Discharge (Ca-HCO₃-SO₄, pH 7)

- Adsorption to Iron Oxide Surfaces
- Exchange Reactions on Carbonate and Clay Mineral Surfaces
- Precipitation of Metal Carbonate Minerals

2,000 Feet
PHAST Model Results
Phase 1: 10 years (~1980)
PHAST Model Results
Phase 1: 20 years (~1990)

Distance from Mine Workings Discharge into Boone Aquifer (ft)

Cadmium, Lead, Arsenic, Zinc Concentration (mg/L)
PHAST Model Results
Phase 1: 40 years (~2010)
PHAST Model Results
Phase 2 Sooner: 5 years

Zinc Concentration (mg/L)
Cadmium, Lead and Arsenic Concentration (mg/L)
Distance from Mine Workings Discharge into Boone Aquifer (ft)
PHAST Model Results
Phase 2 Sooner: 25 years

Distance from Mine Workings Discharge into Boone Aquifer (ft)

Cadmium, Lead, Arsenic, Zinc Concentration (mg/L)
Conclusions: Geochemistry

• Trace metal minerals and salts dissolve during slurry process
• Injected slurry temporarily increases metals concentrations in mine pool
• Concentrations return to original levels after injection stops (trapped in fines)
• Injection expected to have little effect on discharge to Boone Aquifer
  – Higher concentrations temporary
  – High dilution in mine workings
  – Further attenuation after discharge
Questions?
Groundwater Flow Directions
Piper Diagram

Key to Water Sources
- Tailings Pond
- Sandscrew Discharge
- Rubidoux
- Mine Pool
- Chat Pile
- Boone
Boone Groundwater Chemistry
Mine Pool Water Chemistry
Rubidoux Groundwater Chemistry
PHAST Model

- Alternative to use of $K_d$ for adsorption by explicitly modeling adsorption of metals to mineral surfaces
- Database contains expressions for adsorption to hydrous ferric oxides, the most common adsorbent
- Can add published expressions for other minerals (carbonates used in this study)
- Measured or assumed mineral concentrations provide more realistic ceiling for adsorption reactions
  - $K_d$ assumes unlimited adsorption capacity
Dilution from Sooner Location
Dilution from Sooner Location

[Graph showing dilution over time]
Observed Data: Douthat
Observed Data: Douthat