The Aquifer Solid Phase: Reactive Minerals and Their Effect on Remedial Success

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Outline

• Definitions: Solid Phase, Reactive Mineral
• Examples of Reactive Minerals
• Properties of Reactive Minerals
• Analytical Techniques + Limitations
• Case Studies
• Remedial Considerations
• Questions/Comments?
Definition – Aquifer Solid Phase

Soil Sample ≠ Solid Phase Characterization

BUT

Solid Phase Characterization = Soil Sample
Definition – Reactive Mineral

• Minerals that dissolve and/or re-precipitate within a human time-scale in response to changes to pH, redox, or solution composition

• Control dissolved concentration of some metals/anions

• Adsorbent surface for other metals

• Minerals that reach equilibrium with the groundwater composition at the pH and $E_H$ of the aquifer system

• Sources and sinks
Reactive Mineral Examples

- **Adsorbents**
  - Iron oxyhydroxides: ferrihydrite [Fe(OH)$_3$], goethite [αFeOOH], etc
    - Hydrous ferric oxide (HFO) minerals
    - Manganese oxides: pyrolusite [MnO$_2$]
    - Aluminum hydroxide: gibbsite [Al(OH)$_3$]
  - Dzombak – up to 600m$^2$/g surface area for ferrihydrite!
  - Stage 8 Amendments to BC CSR
Reactive Minerals - Adsorbents

General Affinity of Dissolved Species for Fe(OH)$_3$

\[
\begin{align*}
\text{As}^{5+} &= \text{Cu}^{2+} = \text{Be}^{2+} = \text{Pb}^{2+} = \text{PO}_4^{3-} \\
> \text{Zn}^{2+} > \text{Cd}^{2+} > \text{As}^{3+} > \text{Ni}^{2+} > \text{SO}_4^{2-} \\
>> \text{Ba}^{2+} >> \text{Ca}^{2+} >> \text{B}^{3+}
\end{align*}
\]
Reactive Mineral Examples

• **Solubility Controls**
  • Salts: halite \([\text{NaCl}]\), \(\text{MgCl}_2\), \(\text{KCl}\), gypsum \([\text{CaSO}_4 \cdot 2\text{H}_2\text{O}]\)

• **Buffering Agents**
  • Limestone: calcite \([\text{CaCO}_3]\), dolomite \([\text{CaMg(CO}_3)_2]\)
Reactive Mineral Examples

• Acid Rock Drainage
  • Sulphides: pyrite $[\text{FeS}_2]$, galena $[\text{PbS}]$, sphalerite $[(\text{Zn,Fe})\text{S}]$, etc

• Acid Rock Drainage is a result of oxidation of reactive minerals

• Metals plume after injection of chemical oxidant?
Reactive Mineral Examples

• Honourable mention to:
  • Clay minerals
  • Organic Carbon (i.e. foc)
  • Both adsorbents (inorganic and organic, respectively)
  • Not technically reactive minerals, but important solid phase constituents to understand
Properties of Reactive Mineral

• Factors that influence mineral reactivity
  • Structure: crystalline, cryptocrystalline, amorphous
    • Surface area
  • Reaction rims
  • Solution composition
  • pH and redox
Analytical Techniques

- Batch sequential extraction (BCR procedure)
- Column sequential extraction
- Polished thin-sections
- XRD
- SEM-EDS
- QEMSCAN
Batch Sequential Extraction

- BCR Procedure – EU methodology
- Extraction solutions
  - 1 – acetic acid: water, exchangeable and acid soluble
  - 2 – hydroxylammonium chloride: reducible
  - 3 – hydrogen peroxide: oxidizable
  - 4 – ammonium acetate: aqua regia
- Total reactive mineral concentrations
- Some math/stoichiometry to calculate [mineral]
Column Sequential Extraction

- Modified Tessier
  - 1 – DI water: water soluble minerals
  - 2 – ammonium chloride: exchangeable cations
  - 3 – sodium acetate + acetic acid: carbonates
  - 4 – ammonium oxalate + oxalic acid: oxides/hydroxides

- Mimics reactions along a flow path
- Accounts for reaction rim and reaction kinetics
- Mineral stability across range of geochemical conditions
Column Sequential Extraction
Polished Thin-sections
XRD
<table>
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<tr>
<th>Mineral Name</th>
<th>Approximate Mineral Formula</th>
<th>TW15 112</th>
<th>TW15 122</th>
<th>TW15 132</th>
<th>MW15 142</th>
<th>TW15 152</th>
<th>TW15 162</th>
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<tbody>
<tr>
<td>Amphibole</td>
<td>Ca$_2$(Mg,Fe)$_5$(OH)$_2$(Si$<em>4$O$</em>{11}$)$_2$</td>
<td>2.5</td>
<td>3.6</td>
<td>8.7</td>
<td>4.9</td>
<td>5.5</td>
<td>4.5</td>
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<tr>
<td>Calcite</td>
<td>CaCO$_3$</td>
<td>5.8</td>
<td>0.3</td>
<td>0.5</td>
<td>0.0</td>
<td>0.0</td>
<td>3.0</td>
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<tr>
<td>Chlorite</td>
<td>(Mg,Fe)$_6$(Si,Al)$<em>4$O$</em>{10}$(OH)$_8$</td>
<td>3.7</td>
<td>3.0</td>
<td>0.9</td>
<td>0.3</td>
<td>1.0</td>
<td>2.9</td>
</tr>
<tr>
<td>Epidote</td>
<td>Ca$_2$Al$_2$O$_6$.FeOH(Si$_2$O$_7$)(SiO$_4$)</td>
<td>1.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.1</td>
<td>0.7</td>
<td>0.0</td>
</tr>
<tr>
<td>K-feldspar</td>
<td>KAlSi$_3$O$_8$</td>
<td>0.4</td>
<td>1.1</td>
<td>0.3</td>
<td>6.0</td>
<td>2.0</td>
<td>0.6</td>
</tr>
<tr>
<td>Magnetite</td>
<td>Fe$_3$O$_4$</td>
<td>0.6</td>
<td>0.4</td>
<td>0.6</td>
<td>0.6</td>
<td>0.0</td>
<td>3.0</td>
</tr>
<tr>
<td>Mica</td>
<td>KMg$_3$(Si$<em>3$Al)O$</em>{10}$(OH)$_2$</td>
<td>0.8</td>
<td>0.1</td>
<td>0.0</td>
<td>0.2</td>
<td>0.4</td>
<td>0.0</td>
</tr>
<tr>
<td>Plagioclase</td>
<td>(Na,Ca)(Al,Si)$_4$O$_8$</td>
<td>48.4</td>
<td>50.0</td>
<td>46.2</td>
<td>54.1</td>
<td>55.9</td>
<td>42.9</td>
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<td>Pyroxene</td>
<td>Ca$_2$(Mg,Fe)$_5$(OH)$_2$(Si$<em>4$O$</em>{11}$)$_2$</td>
<td>0.0</td>
<td>2.6</td>
<td>1.4</td>
<td>2.6</td>
<td>1.2</td>
<td>2.9</td>
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<td>Quartz</td>
<td>SiO$_2$</td>
<td>36.8</td>
<td>38.8</td>
<td>41.3</td>
<td>31.3</td>
<td>33.4</td>
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<tr>
<td>Sphalerite</td>
<td>ZnS</td>
<td></td>
<td></td>
<td></td>
<td>0.1</td>
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<td></td>
</tr>
</tbody>
</table>
QEMSCAN – Automated SEM-EDS
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Analytical Limitations

- Sample collection, preservation, preparation (nitrogen!)
- Sample size/volume
- Natural heterogeneity (nugget effect)
- Crystalline vs Amorphous
- Resolving mineralogy from EDS
- Mineralogist/Petrologist
Case Studies

• Reactive Minerals as Source
• Reactive Minerals as a Sink
• Reactive Minerals as Sink → Source
• All Sites are confidential
Case Study 1 - Source

- WaterTech 2015 presentation
- Multiple dissolved metals plume in tidally influenced Industrial Site – Steel and wire manufacturer
- Source and Release Mechanism(s)
  - B, Zn and sulphuric acid used at Process Area; but
  - Al, B, Cd, Cu, Ni and Zn in groundwater
- Source of Al, Cd, Cu and Ni?
Case Study 1 - Source
Case Study 1 - Source

- Analytical results indicated:
  - Dissolved iron generally <DL
  - DO ~ 3 mg/L
  - pH <4 in vicinity of Process Area
- Gibbsite [Al(OH)_3] is an adsorbent and exhibits amphoteric behavior
  - Soluble at pH ~<6 and ~>8.5
  - Low pH (acidic dissolution) inferred release mechanism
Case Study 1 - Source

• Source 1 – Chemical Leak through Process Area Floor, contaminating groundwater with B, Zn and acidity

• Source 2 – Acidic dissolution of gibbsite and release of metals adsorbed onto mineral surface

• **Reactive Minerals as a Secondary Source of GW contamination**
Case Study 1 - Source
Case Study 1 - Summary

- Reactive Minerals were source of dissolved metals
- Reacted to pH change (pH <4)
- Acidic dissolution
- Stop acid leak, pH buffers, gibbsite re-precipitates, metals re-adsorb
Case Study 2 - Sink

• Former Industrial Facility adjacent to river
  • Freshwater aquatic habitat – fish rearing
• Dissolved metals plume (primarily copper)

• Is plume at steady state? – limited temporal and spatial data
• Will concentrations at receptor get worse?
Case Study 2 - Sink
Case Study 2 - Sink

- Collected samples for BCR analysis along flow path
  - Ferrihydrite and calcite molar concentrations!
- Prepared reactive transport model using PHREEQC
  - Ferrihydrite and calcite set as equilibrium phases
- Predict long-term behavior of plume and concentration at receptor
  - \([\text{Cu}]\) to increase by >5x!
Case Study 2 - Sink

Cell length = 12.5 m
Flow path length = 750 m
Figure A: Copper Plume Centreline Concentrations Over Time
Case Study 2 - Sink

- Proposing to inject ferric sulphate
- Precipitate iron oxyhydroxides
- Adsorb metals = decrease dissolved concentration
  - $Fe_2(SO_4)_3 + 4.5H_2O \rightarrow 2Fe(OH)_3 + 3H_2SO_4$
    - Reaction needs buffering
- Protect Fish Habitat!
Case Study 2 - Sink

Cell length = 12.5 m
Flow path length = 750m

Scenario 1: 0.395
Scenario 2: 0.395
Scenario 3: 0.395
Scenario 4: 0.384
Scenario 5: 0.2811
Scenario 6: 0.2811
Scenario 7: 0.285
Scenario 8: 0.230
Case Study 2 - Summary

• Metals being “flushed” by clean up-gradient water resulting in migration of plume mass over time
• Inject ferric sulphate to precipitate ferrihydrite
• Reaction needs oxygen and buffering
• Model if sufficient calcite or if need to inject NaOH

• Stay tuned! RemTech2017?
Case Study 3 – Sink to Source

• Former mining site – sulphide minerals
• Multiple dissolved metals plume (Cu, Cd, Ni, Pb, Zn)
• Concentrations > 100,000 µg/L
• Tidally influenced Permeable Reactive Barrier (PRB)
• Treatment mechanism
  • Sulphate reduction followed by metal sulphide precipitation, carbonate precipitation, and adsorption onto iron oxyhydroxide minerals
Case Study 3 – Sink to Source

- PRB near end of design life (depleted reactive media)
- Observed dissolved metals rebound d/g of PRB
- Secondary source or re-dissolution of sulphides?
- To what extent are secondary mineral precipitates stable as PRB loses reactivity?
Case Study 3 – Sink to Source

• Challenges
  • PRB relies on anoxic conditions. How to sample?
  • How to evaluate mineral stability/solubility?
  • How to evaluate mineral texture (crystalline, cryptocrystalline, amorphous)

• Solutions
  • Nitrogen during sample collection
  • Custom Column Sequential Extraction (modified Tessier)
  • Thin-sections, XRD, SEM-EDS, QEMSCAN
Case Study 3 – Sink to Source
Case Study 3 – Sink to Source

• Modified Tessier
  • 1 – DI water: water soluble minerals
  • 2 – ammonium chloride: exchangeable cations
  • 3 – sodium acetate + acetic acid: carbonates
  • 4 – ammonium oxalate + oxalic acid: oxides/hydroxides

• Residence Time
**Case Study 3 – Sink to Source**

**PRB Extraction 2 - Exchangeable**

- **Leachable Concentration [ug/L]**
- **Extraction Cycle [#]**

**Contaminants:**
- Copper (Cu)
- Iron (Fe)
- Lead (Pb)
- Nickel (Ni)
- Zinc (Zn)
- Cadmium (Cd)
Case Study 3 – Sink to Source

PRB Extraction 3 - Carbonates

- Copper (Cu)
- Iron (Fe)
- Lead (Pb)
- Nickel (Ni)
- Zinc (Zn)
- Cadmium (Cd)

Leachable Concentration [ug/L]

Extraction Cycle [#]

Residence Time [hr]
Case Study 3 – Sink to Source

PRB Extraction 4 - Reducible

Leachate Concentration [ug/L] vs. Extraction Cycle [#]

- Copper (Cu)
- Iron (Fe)
- Lead (Pb)
- Nickel (Ni)
- Zinc (Zn)
- Cadmium (Cd)
General Affinity of Dissolved Species for Fe(OH)₃

\[
\text{As}^{5+} = \text{Cu}^{2+} = \text{Be}^{2+} = \text{Pb}^{2+} = \text{PO}_4^{3-}
\]

\[
> \text{Zn}^{2+} > \text{Cd}^{2+} > \text{As}^{3+} > \text{Ni}^{2+} > \text{SO}_4^{2-}
\]

\[
>> \text{Ba}^{2+} >> \text{Ca}^{2+} >> \text{B}^{3+}
\]
Case Study 3 – Summary

- Dissolved metals attenuated as carbonates and adsorbed onto iron oxyhydroxides (goethite)
- Exchangeable cations – high ionic strength solution
- Loss of reactivity and daily tidal influence “bumps” metals off of mineral surface into solution
- Reactive Minerals as a source and a sink!
Remedial Considerations

• Reactive Minerals can be sources, sinks or both

• Manipulating pH and $E_H$ of an aquifer for remediation?

• Characterize the Aquifer Solid Phase!
  • Identify minerals incompatible with remedial approach
  • Buffering agents when acidity produced
  • Naturally present adsorbents minerals
Thank you. Questions?

Contact Us

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