What chemical conditions in Iron-Enhanced Sand Filters favor phosphate retention by iron?

Beth Fisher, Joshua Feinberg, University of Minnesota
EPA Section 319 Project: Shingle Creek Biochar/Iron Sand Bacteria Filters
MSRC Proposal:
Which iron minerals in iron-enhanced sand filters remove phosphorous from stormwater runoff?
Electron backscattered image of Fe particle from North Lions Park sand filter

### Metal composition:

<table>
<thead>
<tr>
<th>Material</th>
<th>Percentage Ranges</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metallic Iron</td>
<td>87-93%</td>
</tr>
<tr>
<td>Total Carbon</td>
<td>2.85-3.23</td>
</tr>
<tr>
<td>Manganese</td>
<td>0.14-0.60</td>
</tr>
<tr>
<td>Sulphur</td>
<td>0.067-0.107</td>
</tr>
<tr>
<td>Phosphorous</td>
<td>0.000-0.132</td>
</tr>
<tr>
<td>Silicon</td>
<td>1.0-1.85</td>
</tr>
<tr>
<td>Nickel</td>
<td>0.05-0.21</td>
</tr>
<tr>
<td>Chromium</td>
<td>0.03-0.23</td>
</tr>
<tr>
<td>Vanadium</td>
<td>ND</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>0.08-0.15</td>
</tr>
<tr>
<td>Titanium</td>
<td>0.004-0.1</td>
</tr>
<tr>
<td>Copper</td>
<td>0.11-0.20</td>
</tr>
<tr>
<td>Aluminum</td>
<td>0-0.005</td>
</tr>
<tr>
<td>Cobalt</td>
<td>ND</td>
</tr>
<tr>
<td>Magnesium</td>
<td>0.01</td>
</tr>
<tr>
<td>Boron</td>
<td>0.01</td>
</tr>
<tr>
<td>Zinc</td>
<td>0.01</td>
</tr>
<tr>
<td>Zirconium</td>
<td>0.01</td>
</tr>
</tbody>
</table>
Metal composition:

- Metallic Iron: 87-93%
- Total Carbon: 2.85-3.23
- Manganese: 0.14-0.60
- Sulphur: 0.067-0.107
- Phosphorous: 0.000-0.132
- Silicon: 1.0-1.85
- Nickel: 0.05-0.21
- Chromium: 0.03-0.23
- Vanadium: ND
- Molybdenum: 0.08-0.15
- Titanium: 0.004-0.1
- Copper: 0.11-0.20
- Aluminum: 0-0.005
- Cobalt: ND
- Magnesium: 0.01
- Boron: 0.01
- Zinc: 0.01
- Zirconium: 0.01

Electron backscattered image of Fe particle from North Lions Park sand filter
North Lions Park

\[ \text{Fe}^{3+}_2\text{O}_3 \]
\[ \text{Fe}^{3+}\text{O(OH)} \]

Magnetite
\[ \text{Fe}_3\text{O}_4 \]

\[ \text{Fe}^0 \]

Zoom
Pearlitic Fe
Observed Cast Iron Corrosion Sequence

Zero Valent Iron → Magnetite Fe₃O₄ → Fe³⁺(aq) → Dissolution → Exit filter as solute

Ferrihydrite disordered ~Fe³⁺₂O₃·0.5(H₂O)

Nucleate & grow

Goethite Fe³+O(OH) (radial needles)

Hematite Fe³⁺₂O₃

Lepidocrocite Fe³+O(OH) (fibrous)

Akaganeite Fe³+O(OH) (spindlelike)

Methods: electron microprobe + magnetic mineralogy
Observed Cast Iron Corrosion Sequence

Zero Valent Iron → Magnetite Fe₃O₄ → Fe³⁺(aq) → Dissolution → Ferrihydrite disordered ≈Fe³⁺₂O₃·0.5(H₂O) → Exit filter as solute

Anoxic at any stage → Fe²⁺(aq) → Dissolution → Exit filter as solute

Goethite Fe³⁺·O(OH) (radial needles)

Hematite Fe³⁺₂O₃

Lepidocrocite Fe³⁺·O(OH) (fibrous)

Akaganeite Fe³⁺·O(OH) (spindlelike)

Methods: electron microprobe + magnetic mineralogy
Observed Cast Iron Corrosion Sequence

Zero Valent Iron → Magnetite Fe₃O₄ → Fe³⁺(aq) → Exit filter as solute

Dissolution

Ferrihydrite disordered ~Fe³⁺₂O₃•0.5(H₂O)

Nucleate & grow

Goethite Fe³⁺O(OH) (radial needles)

Hematite Fe³⁺₂O₃

Lepidocrocite Fe³⁺O(OH) (fibrous)

Methods: electron microprobe + magnetic mineralogy
Zero Valant Iron → Magnetite Fe₃O₄ → Fe³⁺(aq) → Ferrihydrite disordered ~Fe³⁺₂O₃•0.5(H₂O) → Exit filter as solute → Hematite Fe³⁺₂O₃

Methods: electron microprobe + magnetic mineralogy
Zero Valant Iron → Magnetite $\text{Fe}_3\text{O}_4$ → Anoxic at any stage → Fe$^{2+}_{(aq)}$ → Dissolution

Exit filter as solute

Nucleate & grow

Goethite $\text{Fe}^{3+}\text{O(OH)}_3$ (radial needles)

Lepidocrocite $\text{Fe}^{3+}\text{O(OH)}_2$ (fibrous)

Akaganeite $\text{Fe}^{3+}\text{O(OH)}_2$ (spindlelike)

Methods: electron microprobe + magnetic mineralogy

Inundated IESF

P exporting $\times$
Mechanisms for P trapping by Fe

**Option 1**
It can *precipitate* a new mineral that sequesters P
Vivianite, Fe$_2$(PO$_4$)$_2$·8H$_2$O
Strengite, Fe$_2$PO$_4$·2H$_2$O

**Option 2**
*Adsorption* of P via processes like
- Anion exchange
- Ligand exchange
- Cation bridging
Mechanisms for P trapping by Fe

**Option 1**
It can *precipitate* a new mineral that sequesters P
- Vivianite, $\text{Fe}_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$
- Strengite, $\text{Fe}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$

**Option 2**
*Adsorption* of P via processes like
- Anion exchange
- Ligand exchange
- Cation bridging
Adsorption

*Adsorption* of P via processes like
- Anion exchange
- Ligand exchange
- Cation bridging

Depends on *reactive surface area* and *pH*. 
Phosphorus occurs as a phosphate ion that changes with pH

\[
\begin{align*}
&\text{H}_3\text{PO}_4 \\
&\text{H}_2\text{PO}_4^- \\
&\text{HPO}_4^{2-} \\
&\text{PO}_4^{3-}
\end{align*}
\]

(pH: 2.12)
(pH: 7.21)
(pH: 12.67)
# Phosphate sorption capacity

<table>
<thead>
<tr>
<th>Category</th>
<th>Material</th>
<th>PO$_{4}^{3-}$-P/g (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Zero-Valent Iron Metal</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.20-23.62 (Almeelbi et al., 2014)</td>
<td>(Nanoscale)</td>
</tr>
<tr>
<td></td>
<td>3.02–19.02 (Cordray, 2008)</td>
<td>(Microscale)</td>
</tr>
<tr>
<td><strong>Iron Oxides - Magnetite &amp; Hematite</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>11.2 mg (Yan et al., 2010)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>19.02 mg (Cordray, 2008)</td>
<td></td>
</tr>
<tr>
<td><strong>Goethite ($\alpha$-FeOOH)</strong></td>
<td>17.3 mg (Chitrakar et al., 2006)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>17.0 mg (Kim et al., 2011)</td>
<td></td>
</tr>
<tr>
<td><strong>Akaganeite ($\beta$-FeOOH)</strong></td>
<td>20.0 mg (Chitrakar et al., 2006)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>22.0 mg (Kim et al., 2011)</td>
<td></td>
</tr>
<tr>
<td><strong>Lepidocrocite ($\gamma$-FeOOH)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>13.0 mg (Kim et al., 2011)</td>
<td></td>
</tr>
<tr>
<td><strong>Active Carbon (‘biochar’)</strong></td>
<td>3.02 mg (Hussain et al., 2011)</td>
<td></td>
</tr>
<tr>
<td><strong>Calcite</strong></td>
<td>3.1 mg (Karageorgiou et al., 2010)</td>
<td></td>
</tr>
<tr>
<td><strong>Quartz</strong></td>
<td>0.43 (Cucarella &amp; Rennman, 2009)</td>
<td></td>
</tr>
</tbody>
</table>

1 mg/g = 1000 ppm
Adsorption Possibility Depends on pH

Point of Zero Charge (PZC) of oxide

pH lower - - - - - - [PZC] - - - - - - pH higher
+ surface charge + [0] - surface charge -
(attracts anions) (attracts cations)
Adsorption Possibility Depends on pH

Point of Zero Charge (PZC) of oxide

pH lower - - - - - - [PZC] - - - - - - pH higher
+ surface charge + [0] - surface charge -
(attracts anions) (attracts cations)

<table>
<thead>
<tr>
<th>Mineral</th>
<th>pH of PZC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnetite Fe₃O₄</td>
<td>6.5</td>
</tr>
<tr>
<td>Goethite/ Lepidocrocite/ Akaganeite α,β,γ-FeOOH</td>
<td>6.7-7.8</td>
</tr>
<tr>
<td>Hematite α-Fe₂O₃</td>
<td>8.5</td>
</tr>
</tbody>
</table>
Adsorption Possibility Depends on pH

Point of Zero Charge (PZC) of oxide

pH lower  [PZC]  pH higher
+ surface charge +  [0]  - surface charge -
(attracts anions)  (attracts cations)

<table>
<thead>
<tr>
<th>Mineral</th>
<th>pH of PZC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnetite Fe$_3$O$_4$</td>
<td>6.5</td>
</tr>
<tr>
<td>Goethite/ Lepidocrocite/ Akaganeite $\alpha,\beta,\gamma$-FeOOH</td>
<td>6.7-7.8</td>
</tr>
<tr>
<td>Hematite $\alpha$-Fe$_2$O$_3$</td>
<td>8.5</td>
</tr>
</tbody>
</table>
Adsorption Strength Depends on Bond Location

Stumm 1992, Fig. 2.4
Adsorption Strength Depends on Bond Location

- diffuse swarm
- outer-sphere
- inner-sphere
- surface hydroxyl

Stumm 1992, Fig. 2.4
Future work

Additional seasons of monitoring to observe chemistry, pH, oxygen/redox status, iron aging, and to link P removal with geochemistry.

Microbiology is clearly important for IESFs and has not been comprehensively evaluated.

Filter longevity, failure triggers, and decommissioning require more biogeochemical evaluation.
How stable is the metal?

We can use magnetic susceptibility ($\chi$) as a tracer of the metal in these filters.

$\chi_{\text{filter metal}} = 6.2 \times 10^{-4} \ \text{m}^3\text{kg}^{-1}$

$\chi_{\text{filter sand}} = 4.3 \times 10^{-7} \ \text{m}^3\text{kg}^{-1}$

$\chi_{\text{magnetite}} = 2 \times 10^{-4} \ \text{m}^3\text{kg}^{-1}$

$\chi_{\text{hematite, goethite}} = 1 \text{ to } 20 \times 10^{-7} \ \text{m}^3\text{kg}^{-1}$

$\chi_{\text{quartz, feldspar}} = -0.5 \times 10^{-8} \ \text{m}^3\text{kg}^{-1}$
How stable is the metal?

Corning™ Falcon™ polypropylene 50 mL centrifuge tube. Hydrophobic, biologically inert surface. Markings show 5 mL increments.

22 to 26 g of iron enhanced sand filter media

VWR International quantitative grade 474 filter paper for retaining particles >5-10 µm

Polyethylene flat-top screw cap with drainage holes.

Figure 1. Experimental design for the aging of iron enhanced sand filter media. Approximately 50 mL of tap water was allowed to drain through the filter media each business day. Samples were allowed to dry over weekends. This design allows for periodic measurements of magnetic susceptibility without disturbing the filter media. At the end of the experiment, samples were embedded with epoxy to create thin sections for microscopic analysis.

Herrera Aging Experiments

Days

Magnetic Susceptibility, m³/kg

0.00014
0.00012
0.00010
0.00008
0.00006
0.00004

0 20 40 60 80 100
How stable is the metal?

Low temperature SQUID magnetometry shows that this process is accompanied by the development of magnetite, hematite, and Fe-oxyhydroxides like goethite, lepidocrocite, and akaganeite.
Pearlitic texture in steel showing intergrowths of BCC iron (light) and cementite (Fe₃C, dark). This texture is common in all steels cooled in air from above 725°C.

The intergrowths give the steel mechanical properties between the soft-ductile iron and the hard brittle cementite.

C, Mn and Cr tends to partition in the cementite, Al and Si partition into the iron.
### How does pearlitic steel corrode?

<table>
<thead>
<tr>
<th>Type of corrosion</th>
<th>Conditions</th>
<th>Composition of oxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrochemical</td>
<td>Oxygenated water</td>
<td>Goethite, Lepidocrocite</td>
</tr>
<tr>
<td></td>
<td>Sea water</td>
<td>Magnetite, Lepidocrocite, Goethite, Akaganeite</td>
</tr>
<tr>
<td></td>
<td>High SO₂</td>
<td>Mostly Goethite</td>
</tr>
<tr>
<td></td>
<td>High Cl⁻</td>
<td>Mostly Akaganeite</td>
</tr>
<tr>
<td>Thermal</td>
<td>Air, room temperature</td>
<td>Magnetite, Maghemite</td>
</tr>
<tr>
<td></td>
<td>Air, 250-550°C</td>
<td>Magnetite, Hematite</td>
</tr>
<tr>
<td></td>
<td>Air, 600°C</td>
<td>Wustite, Magnetite, Hematite</td>
</tr>
</tbody>
</table>

White et al., 2016
Why does it matter which form of FeOOH is present?

• Each mineral has a different P sorption capacity as a function of pH
• Each mineral has a different pH value for its point of zero charge
• Not all minerals are “re-usable” after desorption
Mineral Precipitation

Vivianite

\[ 3\text{Fe}^{2+} + 2\text{HPO}_4^{2-} + 8\text{H}_2\text{O} + \text{H}^+ \rightleftharpoons \text{Fe}_3(\text{PO}_4)_2\cdot8\text{H}_2\text{O} \]

**Conditions:** anoxic, no S, low Eh (-400 to -100 mV),
moderately high P,
reluctant to form, even when thermodynamically expected

**Stability:** mobile in soil and sedimentary deposits,
stable if physically immobile in lake bottoms?
Fig. 3. Stability relations of iron phosphates and hydroxides in the absence of H₂S. The chemical constraints on which the field boundaries are based are indicated on the right hand side of the diagram.
Anion Exchange

Diffuse ion

Outer-sphere complex
Anion Exchange

Exchange of ions in outer sphere or diffuse swarm.

Conditions:

• pH and Point of Zero Charge (PZC) of oxide
  - pH lower - - - - - - [PZC] - - - - - - pH higher
  + surface + [0] - surface -
  (attracts anions) (attracts cations)

Example PZCs

• Fe₃O₄  pH= 6.5
• α-FeOOH  7.8
• α-Fe₂O₃  8.5
• Fe(OH)₃ (amorph)  8.5

• Ionic strength & charge density of competing ions
  • Cl⁻ can compete at high concentration

Stability: extremely mobile
Ligand Exchange

\[\equiv \text{FeOH} + \text{H}_2\text{PO}_4^- \rightleftharpoons \equiv \text{Fe} \rightarrow \text{O} \quad \text{O}^- \quad \equiv \text{Fe} \rightarrow \text{O} \quad \equiv \text{Fe} \rightarrow \text{O} \quad \equiv \text{FeOH} \]

\text{metal} \quad \text{ligand}

(Lewis Acid) \quad (Lewis Base)

electron acceptor \quad electron donor

**Conditions:** pH dependence (must be lower than PZC of metal), competition of higher affinity ligands

**Stability:** bidendate (two bonds, as shown) much stronger than single ligand bond, inner-sphere bonds are strong, root exudates have the strength to access this P
Cation Bridging

\[ \equiv\text{FeO}^- + \text{Me}^{2+} + \text{H}_2\text{PO}_4^- \iff \equiv\text{FeO} \rightarrow \text{Me} \rightarrow \text{O} \quad \overset{\text{P}}{\text{O}} \quad + 2\text{H}^+ \]

**Conditions:** pH dependence (must be higher than PZC of metal), or Fe bonded with an organic compound could provide negative surface for bridge, affinity of metal decreases proportional to ionic radius

**Stability:** inner-sphere bonds are strong, root exudates have the strength to access this P
Drying Times and Susceptibility Change

All Herrera Samples

Change in the rate of iron loss, % per day

Length of Drying, Days
Eh-pH stability zones of Fe and P

Fig. 3. Stability relations of iron phosphates and hydroxides in the absence of H₂S. The chemical constraints on which the field boundaries are based are indicated on the right hand side of the diagram.

Nriagu 1972, GCA
Anion Exchange

Diffuse ion

Outer-sphere complex
Anion Exchange

Exchange of ions in outer sphere or diffuse swarm.

Conditions:
- pH and Point of Zero Charge (PZC) of oxide
  - pH lower - - - [PZC] - - - pH higher
  - + surface + [0] - surface -
  - (attracts anions) (attracts cations)

Example PZCs
- Fe$_3$O$_4$ pH = 6.5
- α-FeOOH 7.8
- α-Fe$_2$O$_3$ 8.5
- Fe(OH)$_3$ (amorph) 8.5

- Ionic strength & charge density of competing ions
  - Cl$^-$ can compete at high concentration

Stability: extremely mobile
Ligand Exchange

\[ \equiv \text{FeOH} + \text{H}_2\text{PO}_4^- \rightleftharpoons \equiv \text{Fe} \equiv \text{O} \equiv \text{O}^- + 2\text{H}_2\text{O} \]

**Conditions:** pH dependence (must be lower than PZC of metal), competition of higher affinity ligands

**Stability:** bidendate (two bonds, as shown) much stronger than single ligand bond, inner-sphere bonds are strong, root exudates have the strength to access this P (Lewis Acid) electron acceptor (Lewis Base) electron donor
Cation Bridging

\[ \equiv \text{FeO}^- + \text{Me}^{2+} + \text{H}_2\text{PO}_4^- \rightleftharpoons \equiv \text{FeO} - \text{Me} - \text{O} \neq \text{P} \neq \text{O} + 2\text{H}^+ \]

**Conditions:** pH dependence (must be higher than PZC of metal), or Fe bonded with an organic compound could provide negative surface for bridge, affinity of metal decreases proportional to ionic radius

**Stability:** inner-sphere bonds are strong, root exudates have the strength to access this P
Fig. 3. Stability relations of iron phosphates and hydroxides in the absence of $\text{H}_2\text{S}$. The chemical constraints on which the field boundaries are based are indicated on the right hand side of the diagram.
Phosphorus occurs as a phosphate ion

Orthophosphate ("reactive")
Measured from unfiltered sample;
Includes dissolved and suspended orthophosphate, organic P.
Reported in mg/L as P.

TP (total phosphorus)
Measured from unfiltered sample, but digested to convert all forms to orthophosphate.
Reported in mg/L as TP.

Dissolved Phosphorus
Measured from filtered sample (0.45μm);
Includes only fraction of phosphorus in solution in the water.

\[
\begin{align*}
H_3PO_4 & \\
H_2PO_4^- & \\
HPO_4^{2-} & \\
PO_4^{3-} & 
\end{align*}
\]