The Activated Iron Technology: A New Chemical Water Treatment Platform

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Overview

• Activated Iron vs. Traditional Zero-Valent Iron
  – ZVI (or Fe$^0$) chemistry
  – Potential and obstacles: passivation issues
  – Our solution to overcome passivation
  – Lab mechanistic, kinetics, and treatability studies

• Collaborations with industrial partners
  – Pilot (1-2 gpm) tests (2009-2015)
  – Pre-commercial scale demonstrations
    • Pironox™ Advanced Reactive Media System (Evoqua)
    • 25 gpm (136 m$^3$/d) at a power plant
    • 15 gpm (82 m$^3$/d) at a refinery
ZVI-Based Permeable Reactive Barrier

• ZVI as reactive media for environ. remediation
  — inexpensive, widely available
  — versatile

• Became a hot research topic since early 1990s
  — many successes in groundwater remediation
How Fe\(^0\) Removes Contaminants?

- **Redox reaction**
  - \(\text{Fe}^0\) (or derivative \(\text{Fe(II)}\) or \(\text{H}^\bullet\)): e\^- source
  - Contaminants as oxidizing agents
    - Nonmetal Oxyanions: \(\text{NO}_3^-\), \(\text{NO}_2^-\), \(\text{BrO}_3^-\), \(\text{IO}_3^-\)
    - Metal/Metalloids Oxyanions: \(\text{SeO}_4^{2-}\), \(\text{MoO}_4^{2-}\), \(\text{CrO}_4^-\), \(\text{VO}_3^-\)
    - Cationic metals: \(\text{Cu}^{2+}\), \(\text{Hg}^{2+}\)
    - Organic: TCE, TNT, RDX

- **Immobilized through surface adsorption on FeOx produced from iron corrosion**
  - Heavy metals: As
  - Radionuclides: U
ZVI Application: Major Challenges

• How to maintain iron reactivity in aquatic environments?
  • Iron grains rust, form iron oxide coatings, and lose reactivity (become passivated)

• No good solution
  • Acidic pH & regular backwash?
  • Mechanical stripping: sonication?
  • Nano-scale ZVI?
Mechanistic and Kinetics Studies

• Nitrate reduction by Fe$^0$
• Diagnose a key test – Fe$^0$/Nitrate with init. pH = 2.3
• Nitrate removal in three stages
  – Stage 1: Acidic cond.
  – Stage 2: Transition
  – Stage 3: Neutral cond.
• Complex mechanisms
Findings from Mechanistic and Kinetics Studies

- Passivation of Fe\(^0\) may be caused by ferric oxides or amorphous ferrous (oxyhydr)oxides
  - Formed under most natural or engineered aquatic environments
- Magnetite (Fe\(_3\)O\(_4\)) coating on Fe\(^0\) can maintain high Fe\(^0\) reactivity
- Provide external Fe\(^{2+}\) to facilitate transformation of passive ferric oxide coating to a reactive magnetite layer
  - Fe\(^0\) reactivity be sustained
- Propose a semiconducting corrosion model (2000)
Two-layer Semiconducting Corrosion Model (2000)

Fe
0
Fe
2+
Holes
Fe
3+
e
-
1
2
3
4
5
6
7
Fe
0
Fe
3
O
Fe
FeOOH
2O
Liquid
Mechanism: semiconducting corrosion

Fe²⁺/Fe₃O₄ Mechanism
• The fate of Fe²⁺
  • Aq. Fe²⁺ → S.B. Fe²⁺ → Structural Fe(II)/Fe(III)
• Fe²⁺ is not the main e⁻ source, Fe⁰ is.
• Formation of magnetite triggered rapid redox reaction

Rationale/Hypotheses
• Fe₃O₄ (or Fe²⁺Fe³⁺₂O₄) has a metallic-like e⁻ conductivity
• With nitrate, the outer layer of magnetite may be further oxidized to maghemite (γ-Fe₂O₃)
• Maghemite as e⁻ transfer barrier stops the reaction
• Surface-bound Fe²⁺ converts maghemite to magnetite
Heavy Metals in Industrial Wastewater

- **Trace metals**
  - Se, Hg, As, Cr, V, Cu, Zn, Pb, U, Tl
  - flue-gas desulfurization (FGD) wastewater
  - refinery stripped sour wastewater
  - mining wastewater

- **New Regulations**
    - Se < 12 ppb
    - Hg < 0.356 ppb
    - As < 8 ppb
  - State/Local Reg.
ZVI for Wastewater Treatment

• Focus on removing pollutants/impurities from impaired water
  • Industrial wastewaters: Power, Mining, Refinery, etc.
  • Pollutants: Se, As, Cr, Hg, etc.

• Develop the hybrid ZVI/Fe$_3$O$_4$/Fe(II) technology
  • Employ Fe$^{2+}$-Fe$_3$O$_4$ mechanism to prevent or reverse ZVI passivation
  • Discover synergistic effect of ZVI and discrete Fe$_3$O$_4$
  • Use fluidized bed reactor to maintain high reactive solid conc.
  • Create a hybrid reactive system, produced highly reactive secondary species
Activated Iron Technology

• Activated Iron Technology utilizes a series of chemical reactions and mechanisms that in tandem can overcome the passivation of ZVI
  – Increase reaction rate – greater than 99% removal efficiency
  – Reduce ZVI consumption – lower cost
  – Reduce solid waste production – lower cost

\[ \text{sf.rx.ZVI} + \text{Fe}_3\text{O}_4 + \text{Fe(II)} = \text{Activated Iron Media} \]

• A novel high-performance reactor design
• Robust and flexible treatment process configuration
Metallic Iron Powder $\rightarrow$ Activated Iron Media

$\{ \text{sf.r.ZVI} + \text{FeOx} + \text{Fe(II)} \}$

Settling after:

1 min 3 min

The mature reactive solids settle rapidly.
Activated Iron Technology utilizes a series of chemical reactions and mechanisms that in tandem can overcome the passivation of ZVI. 

- Discover synergistic effect between ZVI and \( \text{Fe}_3\text{O}_4 \). 
  - Increase reaction rate
  - Greater than 99% removal efficiency
  - Reduce ZVI consumption
  - Lower cost
  - Reduce solid waste production
  - Lower cost

Activated Iron Media

- A novel high-performance reactor design
- Robust and flexible treatment process configuration
Activated Iron Media vs. ZVI: a $\text{MoO}_4^{2-}$ example

Test conditions:
1. 100 g/L ZVI
2. 100 g/L ZVI + 1 mM Fe$^{2+}$
3. hZVI: 98 g/L ZVI + 2 g/L Fe$_3$O$_4$ + 1 mM Fe$^{2+}$
4. hZVI: 96 g/L ZVI + 4 g/L Fe$_3$O$_4$ + 1 mM Fe$^{2+}$
Activated Iron Technology

A chemical treatment platform that uses reactive power of rapid iron corrosion process to remove various contaminants/impurities from water

Applications:

- Remove Se, Hg, and As from impaired water
- Remove dissolved silica for many industrial water supplies
Field Demonstrations

• Bench-top demonstration at Plant A (October 2009)
• Treating Flue-Gas-Desulfurization Wastewater

Continuous-flow
Treated 30 L/d
Pilot Demo at Power Plants (2011-2015)

Treated 1-2 gpm or 5-10 m³/d
### Activated Iron treatment performance

Table: Removal of contaminants at *Plant A* test (2009)

<table>
<thead>
<tr>
<th>Pollutants</th>
<th>Influent (as total metal)</th>
<th>Effluent</th>
<th>Removal Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selenium</td>
<td>1910 to 2950 ppb</td>
<td>Total Se &lt; 7 ppb</td>
<td>&gt; 99.8%</td>
</tr>
<tr>
<td>Mercury</td>
<td>22 to 61 ppb</td>
<td>Total Hg &lt; 0.005 ppb</td>
<td>&gt; 99.99%</td>
</tr>
<tr>
<td>Arsenic</td>
<td>6.4 to 10.6 ppb</td>
<td>Total As &lt; 0.3 ppb</td>
<td>&gt; 97%</td>
</tr>
<tr>
<td>Cadmium</td>
<td>45 to 73 ppb</td>
<td>Total Cd &lt; 0.3 ppb</td>
<td>&gt; 99%</td>
</tr>
<tr>
<td>Chromium</td>
<td>25 to 55 ppb</td>
<td>Total Cr &lt; 0.6 ppb</td>
<td>&gt; 98%</td>
</tr>
<tr>
<td>Nickel</td>
<td>231 to 266 ppb</td>
<td>Total Ni &lt; 7.0 ppb</td>
<td>&gt; 97%</td>
</tr>
<tr>
<td>Lead</td>
<td>3.3 ppb</td>
<td>Total Pb &lt; 0.08 ppb</td>
<td>&gt; 97%</td>
</tr>
<tr>
<td>Zinc</td>
<td>901 to 1350 ppb</td>
<td>Total Zn &lt; 2.0 ppb</td>
<td>&gt; 99.8%</td>
</tr>
<tr>
<td>Vanadium</td>
<td>17 to 23 ppb</td>
<td>Total V &lt; 0.15 ppb</td>
<td>&gt; 99.8%</td>
</tr>
<tr>
<td>Nitrate</td>
<td>30 ppm Nitrate-N</td>
<td>Nitrate-N &lt; 0.2 ppm</td>
<td>&gt; 99%</td>
</tr>
</tbody>
</table>
## Activated Iron (TAMU Tech) vs. Traditional ZVI (EPRI Report 1017956)

<table>
<thead>
<tr>
<th></th>
<th>Traditional ZVI (EPRI 1017956)</th>
<th>Activated Iron (Texas A&amp;M)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Performance</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Se in treated effluent</td>
<td>ca. 150 ppb</td>
<td>&lt; 10 ppb</td>
</tr>
<tr>
<td>Hg in treated effluent</td>
<td>ca. 100 ppt</td>
<td>&lt; 10 ppt</td>
</tr>
<tr>
<td><strong>Reagent Usage</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZVI ($1,200/ton)</td>
<td>2 g/L</td>
<td>0.1-0.3 g/L</td>
</tr>
<tr>
<td>Acid (35% HCl)</td>
<td>15 g/L</td>
<td>none</td>
</tr>
<tr>
<td>Lime (Ca(OH)(_2))</td>
<td>2.3 g/L</td>
<td>&lt; 0.1 g/L</td>
</tr>
<tr>
<td>Fe(II) salt</td>
<td>ca. 0.05-0.2 g/L</td>
<td></td>
</tr>
<tr>
<td><strong>Solid Waste Production</strong></td>
<td>ca. 10 g/L</td>
<td>&lt; 1 g/L</td>
</tr>
</tbody>
</table>
TCLP test result

Solid waste: highly stable minerals, non-hazardous waste – all samples pass USEPA TCLP test (Toxicity Characteristic Leaching Procedure)

<table>
<thead>
<tr>
<th>Metal</th>
<th>Limits</th>
<th>Sample A (April 2011)</th>
<th>Sample B (June 2011)</th>
<th>Sample C (May 2011)</th>
<th>Units</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver</td>
<td>5</td>
<td>&lt;0.012</td>
<td>&lt;0.012</td>
<td>&lt;0.012</td>
<td>mg/L</td>
<td>EPA 1311/6010</td>
</tr>
<tr>
<td>Arsenic</td>
<td>5</td>
<td>&lt;0.02</td>
<td>0.025</td>
<td>&lt;0.02</td>
<td>mg/L</td>
<td>EPA 1311/6010</td>
</tr>
<tr>
<td>Barium</td>
<td>100</td>
<td>0.169</td>
<td>0.109</td>
<td>2.02</td>
<td>mg/L</td>
<td>EPA 1311/6010</td>
</tr>
<tr>
<td>Cadmium</td>
<td>1</td>
<td>&lt;0.005</td>
<td>&lt;0.005</td>
<td>&lt;0.005</td>
<td>mg/L</td>
<td>EPA 1311/6010</td>
</tr>
<tr>
<td>Chromium</td>
<td>5</td>
<td>&lt;0.003</td>
<td>&lt;0.003</td>
<td>0.0047</td>
<td>mg/L</td>
<td>EPA 1311/6010</td>
</tr>
<tr>
<td>Mercury</td>
<td>0.2</td>
<td>&lt;0.00175</td>
<td>&lt;0.00175</td>
<td>&lt;0.00175</td>
<td>mg/L</td>
<td>EPA 1311/7470</td>
</tr>
<tr>
<td>Lead</td>
<td>5</td>
<td>&lt;0.03</td>
<td>&lt;0.03</td>
<td>0.196</td>
<td>mg/L</td>
<td>EPA 1311/6010</td>
</tr>
<tr>
<td>Selenium</td>
<td>1</td>
<td>&lt;0.036</td>
<td>&lt;0.036</td>
<td>&lt;0.036</td>
<td>mg/L</td>
<td>EPA 1311/6010</td>
</tr>
</tbody>
</table>
Findings from Lab and Field Tests

• The Activated Iron Technology is effective for treating:
  - Se, Hg, U, Tl, As, Cr, Cd, V, Cu, Zn, Pb, Ni, Mo

• A single-stage system with HRT< 1 hr can ensure total Hg < 10 ng/L (ppt), and Cr, As, Pb, and Cd < 1 μg/L (ppb)

• For treating mining wastewater, a single-stage system with HRT=0.5 h is adequate.

• For a refinery stripped sour water, a two-stage system with HRT=2 hr is adequate.

• For a typical FGD wastewater, a 3-stage system with HRT=4 -12 hr is adequate for total Se < 10 ppb.
Robustness

- The Activated Iron Technology remains effective under complex water matrix. Compatible with:
  - High TDS up to 70,000 mg/L
  - Cl\(^-\) up to 20,000 mg/L, SO\(_4^{2-}\) up to 20,000 mg/L
  - Ca\(^{2+}\), Mg\(^{2+}\), Na\(^+\), K\(^+\), Fe\(^{2+}\), Mn\(^{2+}\)
  - Borate, phosphate, nitrate, bromate, iodate, periodate, carbonate, fluoride, bromide, iodide, sulfide, persulfate
  - Dissolved silica up to 300 mg/L
  - phenol, acetate, glucose, sugar
  - Can remove SeCN\(^-\)
Advantages of the Activated Iron Process

• **Simplicity:** Requires no complicated and expensive pretreatments or post-treatments. Can be added to the existing wastewater systems

• **Versatility and Robustness:** A single process removes most concern metals and metalloids from industrial waste streams

• **High removal efficiency:** Se and Hg, below restricted limits

• **Low O&M cost:** Uses common, inexpensive, nontoxic substances (zero-valent iron)

• **Limited sludge production:** Operates at near-neutral pH, which reduces chemical consumption and limits sludge production
Pre-Commercial Scale Demonstrations (by Evoqua Water Technologies LLC)

- Treating FGD Wastewater
- At the Water Research Center (DoE, EPRI, SoCo, SRI), 2014-present
- 25 gpm (130 m³/d)
- Fully scalable to a larger system
- Full process development
Plant B (25gpm) – Metals Removal, 4 Hr HRT

Concentration ppb (capped scale)

Influent | Effluent
---|---
Aluminum | 133 | 6.77
Arsenic | 9.5 | 0.26
Cadmium | 0.26 | 0.11
Chromium | 8.2 | 0.11
Copper | 10.05 | 1.26
Lead | 1.13 | 6.77
Mercury | 4.62 | 0.26
Molybdenum | 0.20 | 6.77
Nickel | 14.40 | 0.0048
Selenium | 4.83 | 0.48
Thallium | 193 | 1.66
Zinc | 1663 | 1.69

Influent: Concentration in the influent stream
Effluent: Concentration in the effluent stream
Pre-commercial Scale Demonstration

• At a Refinery Facility in Colorado
• 5-15 gpm (27-84 m³/d) demo (vs. 200 gpm in full scale)
• Treating Stripped Sour Water
• Main Target: Selenium
  – Reduce ~500 ppb Se to < 4.7 ppb
  – vs. Best previous results > 40 ppb
• 15 months demonstration
  – Meet the target Selenium limit
  – Actual Q: 15 gpm (84 m³/d)
Implications

• Many full-scale commercial applications being planned in several industries
• New benchmarks for future regulations? e.g. Hg<10 ppt, As<1 ppb?

Future work

• Further expand ZVI research in both depth and breadth
• Explore other potentials of the activated iron chemistry
• Continue to support commercialization efforts
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Questions?