The Activated Iron Technology: A New Chemical Water Treatment Platform

Tian C. ZHANG, PhD

Civil Engineering
University of Nebraska

Yongheng HUANG, PhD

Biological and Agricultural Engineering
Texas A&M University
Texas A&M AgriLife Research

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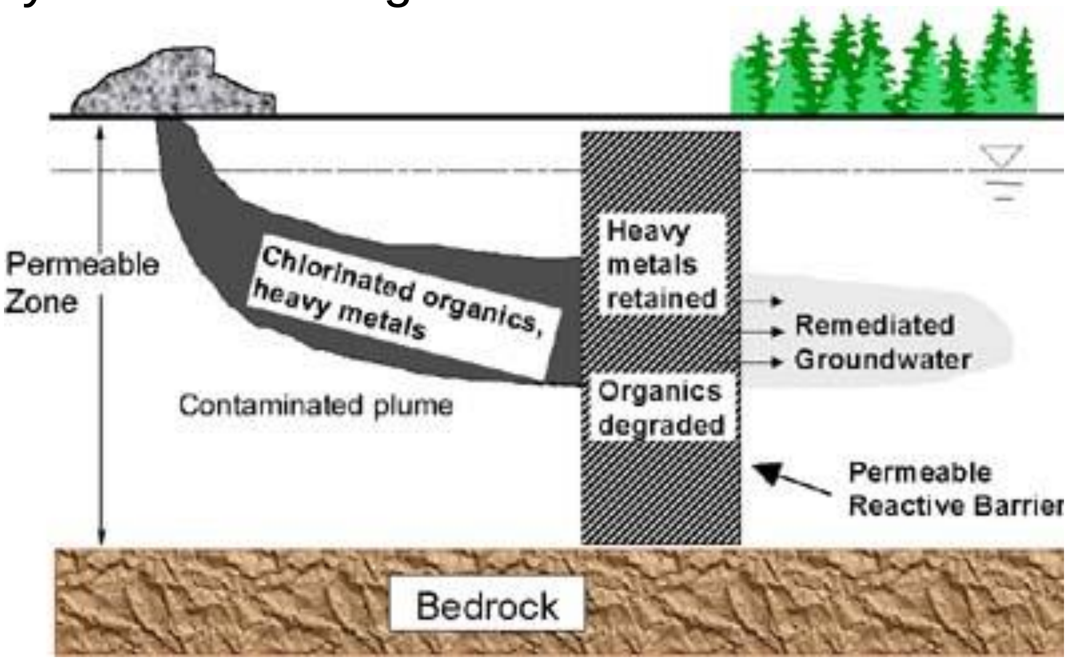
Overview

- **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**
  - **Fe^0** (or derivative **Fe(II)** or **H•**): e^- source
  - Contaminants as oxidizing agents
    - Nonmetal Oxyanions: NO_3^-, NO_2^-, BrO_3^-, IO_3^-
    - Metal/Metalloids Oxyanions: SeO_4^{2-}, MoO_4^{2-}, CrO_4^-, VO_3^-
    - Cationic metals: Cu^{2+}, 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?

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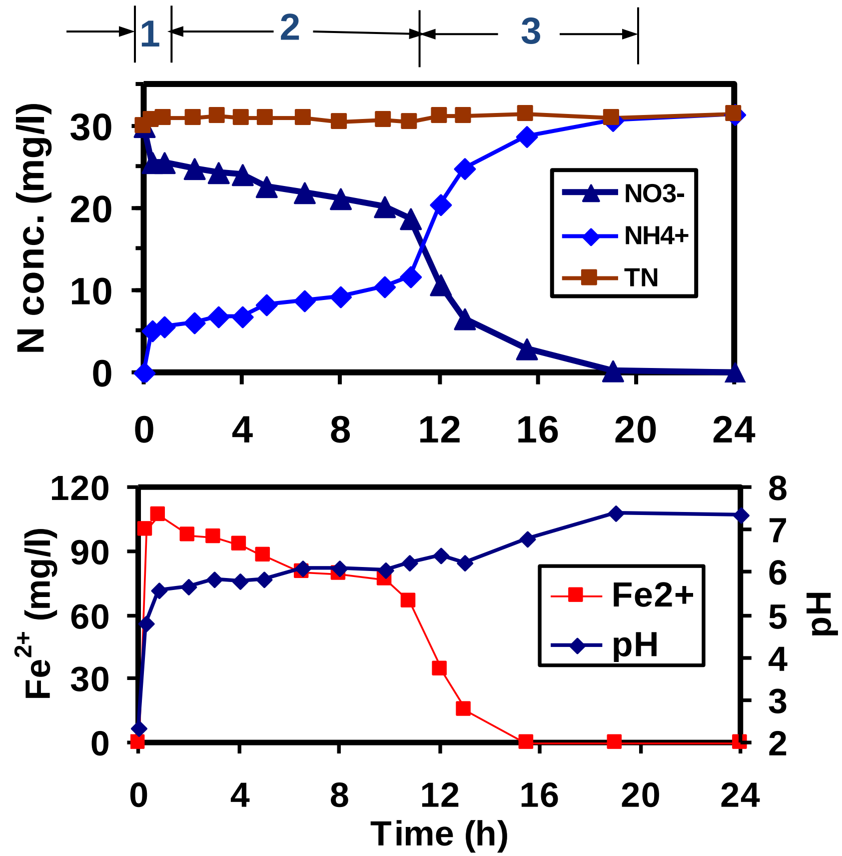
Mechanistic and Kinetics Studies

- 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_3O_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)**

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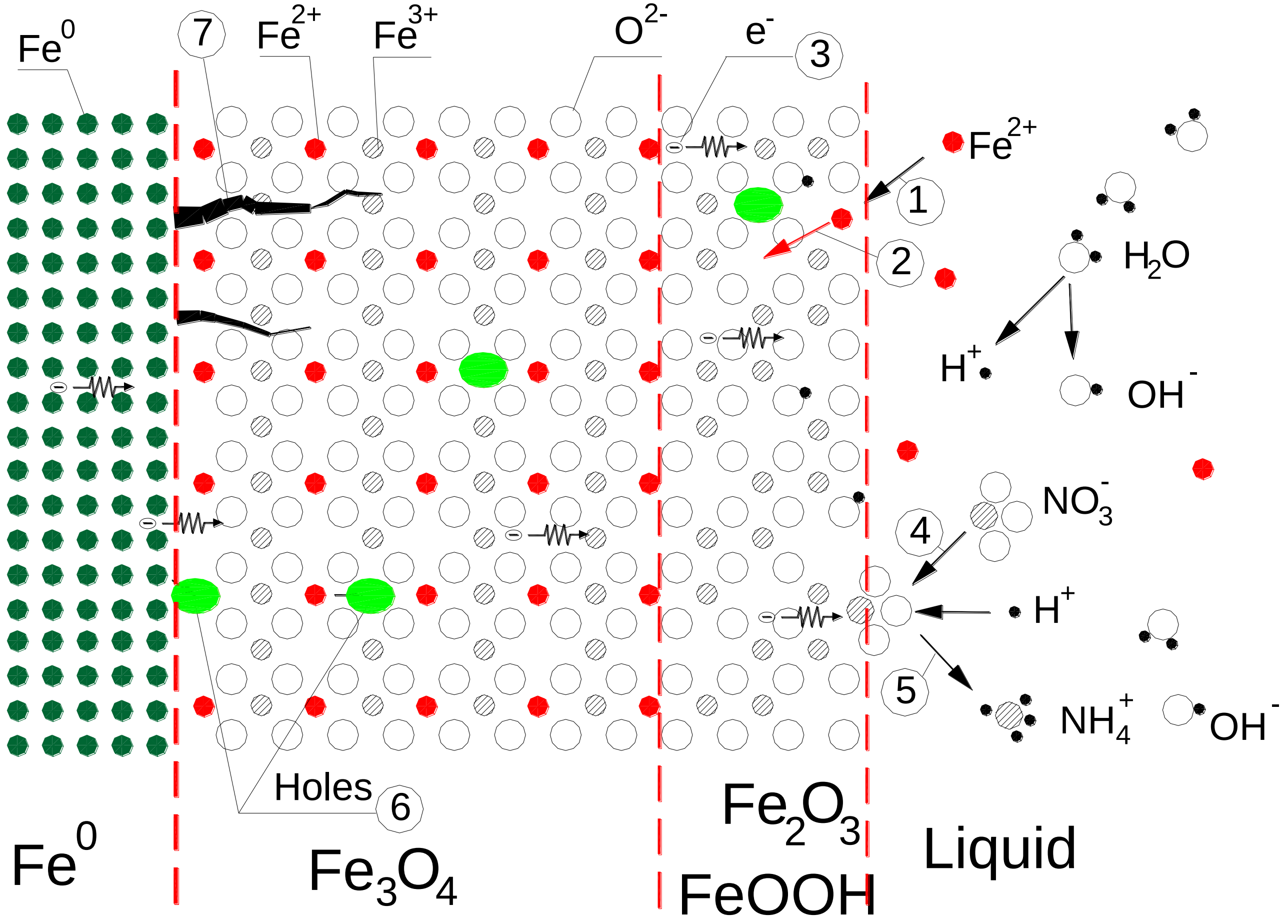
Two-layer Semiconducting Corrosion Model (2000)



Mechanism: semiconducting corrosion

Fe^{2+}/Fe_3O_4 Mechanism

- The fate of Fe^{2+}
  - Aq. Fe^{2+} → S.B. Fe^{2+} → Structural Fe(II)/Fe(III)
- Fe^{2+} is not the main e^- source, Fe^0 is.
- Formation of magnetite triggered rapid redox reaction

Rationale/Hypotheses

- **Fe_3O_4** (or **$Fe^{II}Fe^{III}{}_2O_4$**) has a metallic-like e^- conductivity
- With nitrate, the outer layer of magnetite may be further oxidized to maghemite (γ-Fe_2O_3)
- Maghemite as **e^-** transfer barrier stops the reaction
- Surface-bound Fe^{2+} converts maghemite to magnetite

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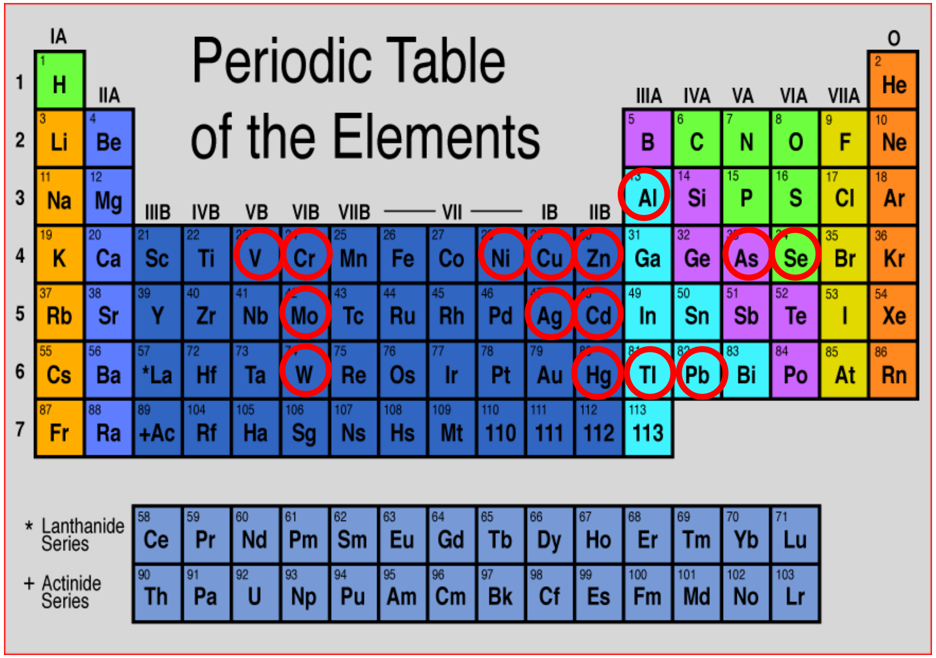
Heavy Metals in Industrial Wastewater

- **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**
  - Effluent Limitations Guidelines by EPA (2015)
    - 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_3O_4/Fe(II) technology**
  - **Employ Fe^{2+}-Fe_3O_4 mechanism to prevent or reverse ZVI passivation**
  - **Discover synergistic effect of ZVI and discrete Fe_3O_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

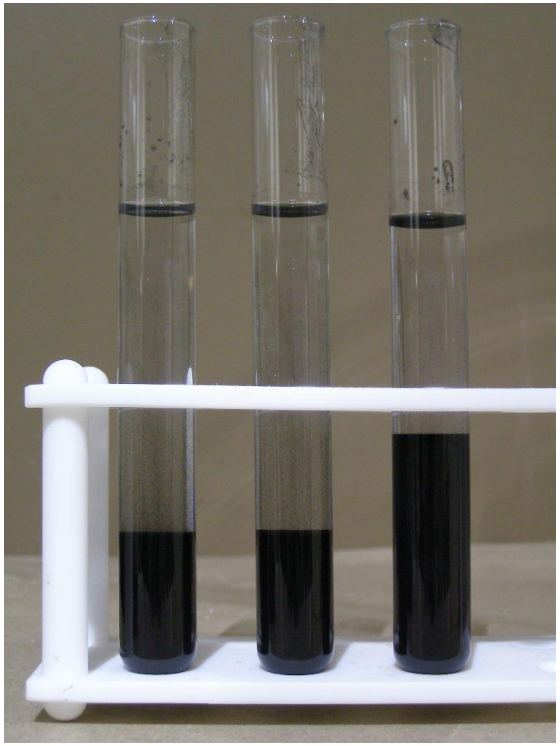
sf.rx.ZVI + Fe_3O_4 + Fe(II) = Activated Iron Media

- A novel high-performance reactor design
- Robust and flexible treatment process configuration

Metallic Iron Powder → **Activated Iron Media**

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

→

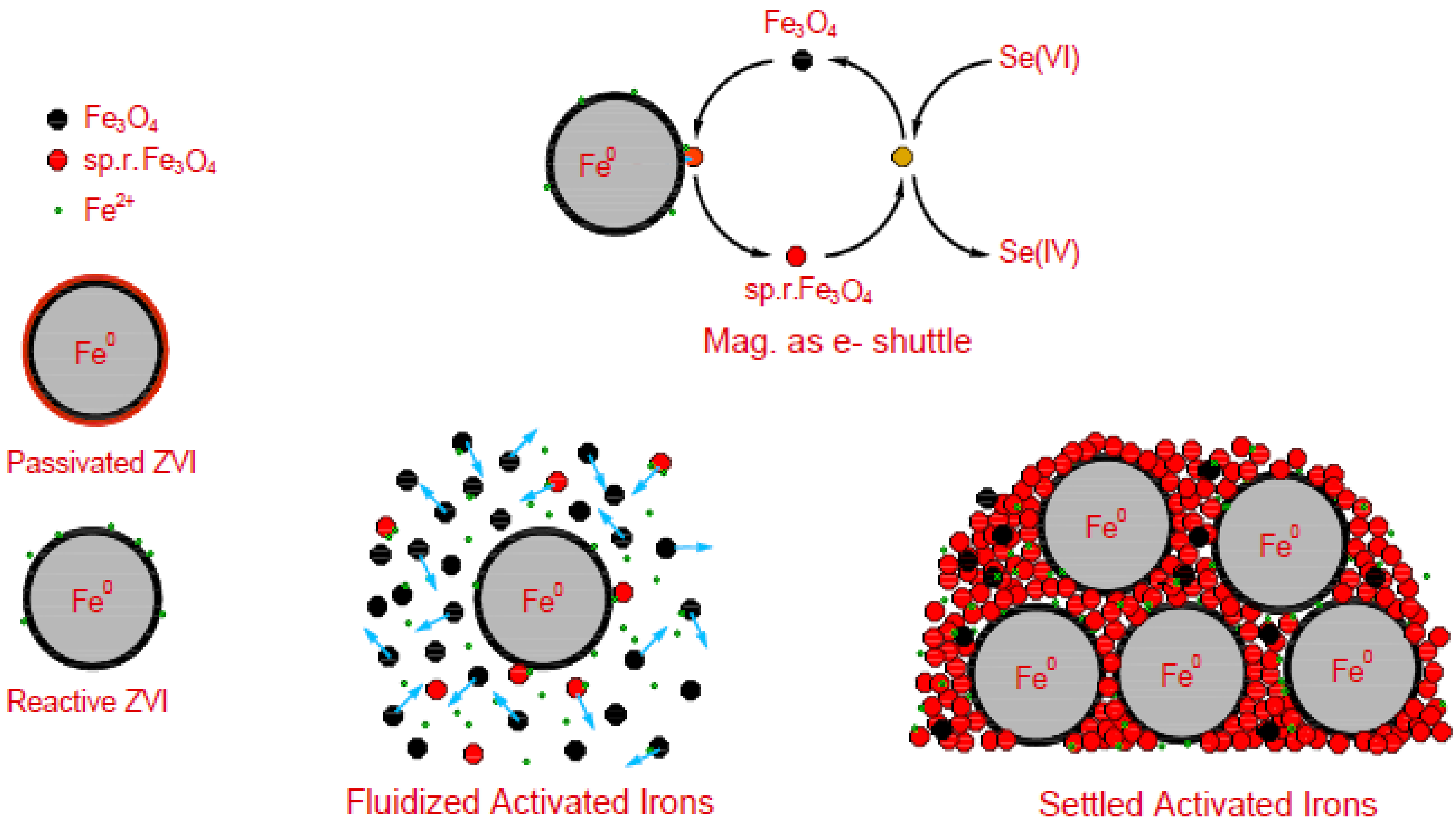


Settling after:

1 min **3 min**

The mature reactive solids settle rapidly.

Activated Iron Media



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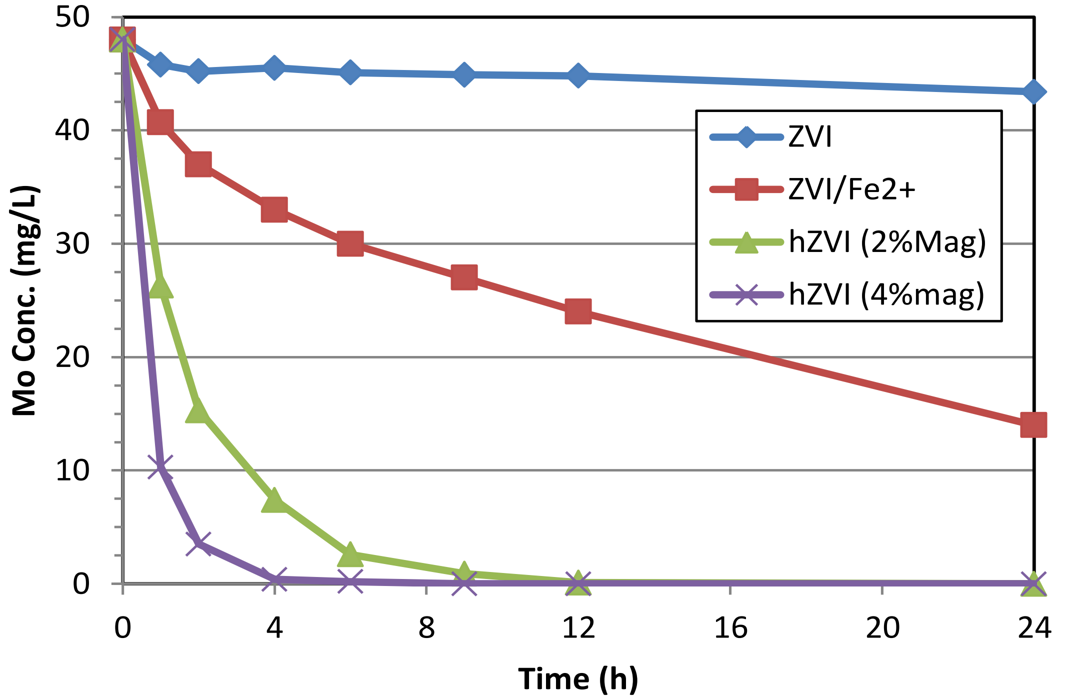
Activated Iron Media vs. ZVI: a MoO_4^{2-} example



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_3O_4 + 1 mM Fe^{2+}
4. hZVI: 96 g/L ZVI + 4 g/L Fe_3O_4 + 1 mM Fe^{2+}

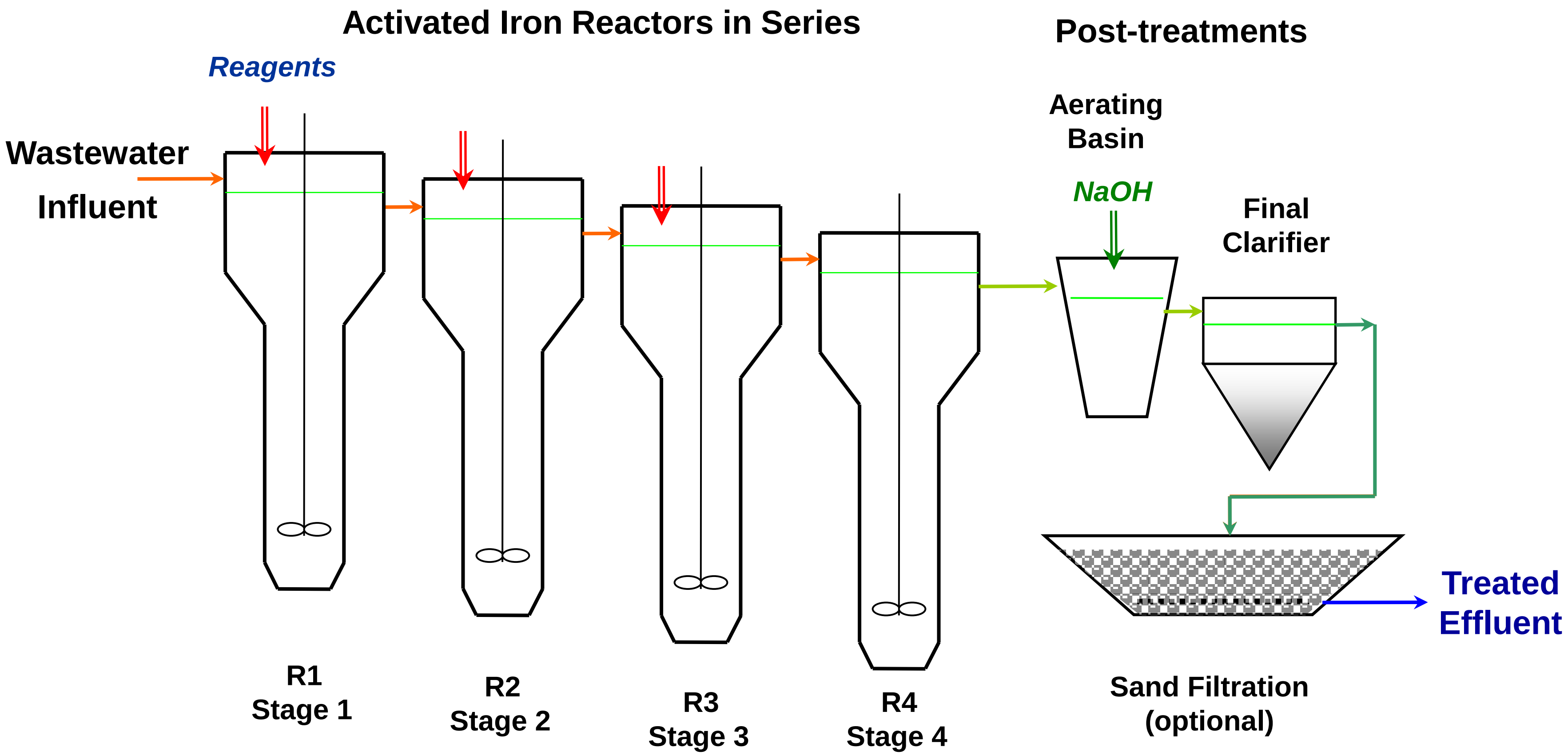
Activated Iron Technology

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

Activated Iron Water Treatment System



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 m^3/d

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Activated Iron treatment performance

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

Pollutants	Influent (as total metal)	Effluent	Removal Efficiency
Selenium	1910 to 2950 ppb	Total Se < 7 ppb	> 99.8%
Mercury	22 to 61 ppb	Total Hg < 0.005 ppb	> 99.99%
Arsenic	6.4 to 10.6 ppb	Total As < 0.3 ppb	> 97%
Cadmium	45 to 73 ppb	Total Cd < 0.3 ppb	> 99%
Chromium	25 to 55 ppb	Total Cr < 0.6 ppb	> 98%
Nickel	231 to 266 ppb	Total Ni < 7.0 ppb	> 97%
Lead	3.3 ppb	Total Pb < 0.08 ppb	> 97%
Zinc	901 to 1350 ppb	Total Zn < 2.0 ppb	> 99.8%
Vanadium	17 to 23 ppb	Total V < 0.15 ppb	> 99.8%
Nitrate	30 ppm Nitrate-N	Nitrate-N < 0.2 ppm	> 99%

Activated Iron (TAMU Tech) vs. Traditional ZVI (EPRI Report 1017956)

	Traditional ZVI (EPRI 1017956)	**Activated Iron (Texas A&M)**
Performance		
Se in treated effluent	ca.150 ppb	**< 10 ppb**
Hg in treated effluent	ca. 100 ppt	**< 10 ppt**
Reagent Usage		
ZVI ($1,200/ton)	2 g/L	**0.1-0.3 g/L**
Acid (35% HCl)	15 g/L	none
Lime ($Ca(OH)_2$)	2.3 g/L	< 0.1 g/L
Fe(II) salt		ca. 0.05-0.2 g/L
Solid Waste Production		
	ca.10 g/L	**< 1 g/L**

TCLP test result

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

Metal	Limits	Results: Sample A (April 2011)	Sample B (June 2011)	Sample C (May 2011)	Units	Method
Silver	5	<0.012	<0.012	<0.012	mg/L	EPA 1311/6010
Arsenic	5	<0.02	0.025	<0.02	mg/L	EPA 1311/6010
Barium	100	0.169	0.109	2.02	mg/L	EPA 1311/6010
Cadmium	1	<0.005	<0.005	<0.005	mg/L	EPA 1311/6010
Chromium	5	<0.003	<0.003	0.0047	mg/L	EPA 1311/6010
Mercury	0.2	<0.00175	<0.00175	<0.00175	mg/L	EPA 1311/7470
Lead	5	<0.03	<0.03	0.196	mg/L	EPA 1311/6010
Selenium	1	<0.036	<0.036	<0.036	mg/L	EPA 1311/6010

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 $SeCN^-$

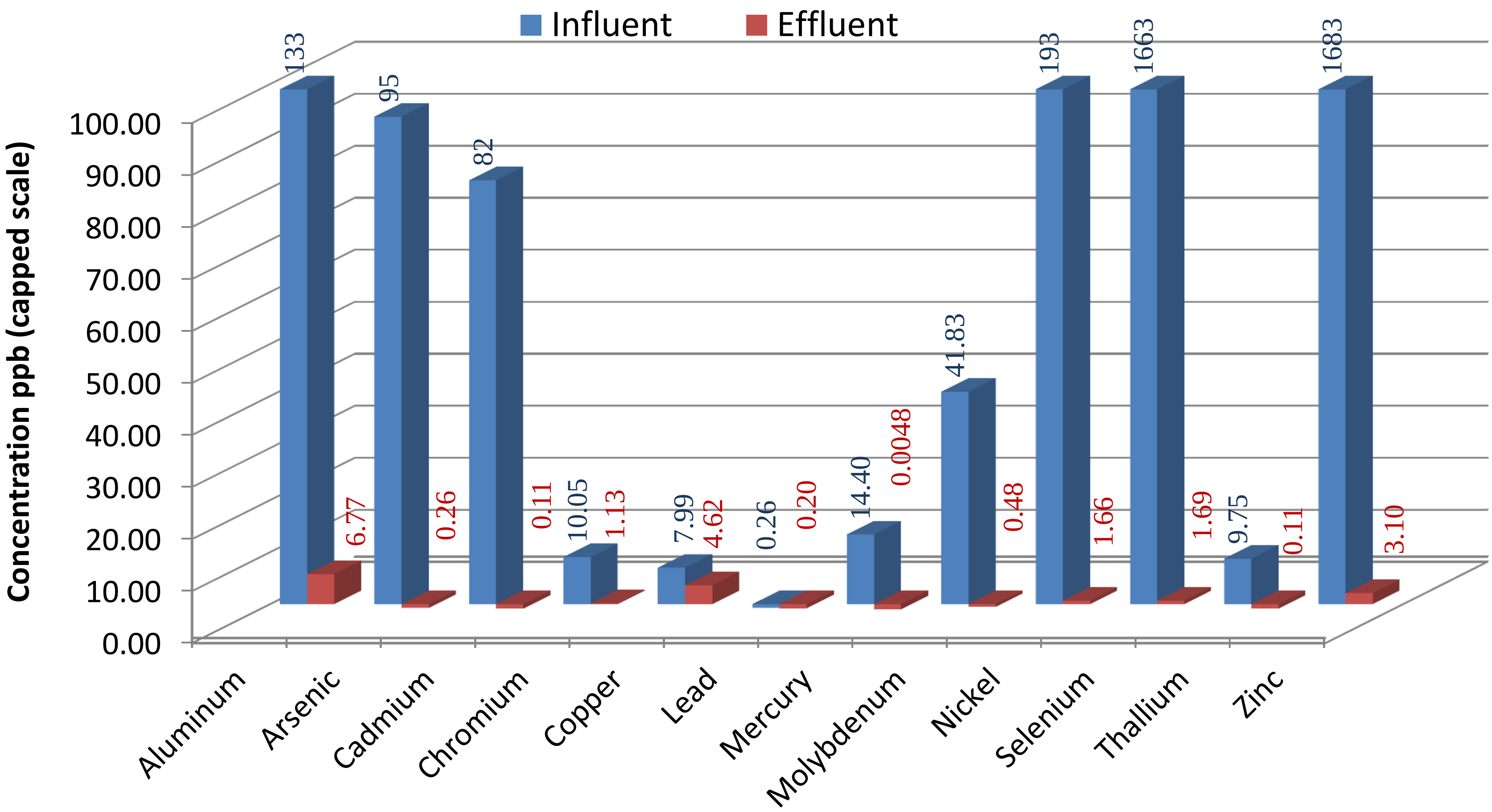
Advantages of the Activated Iron Process

- **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 m^3/d)
- Fully scalable to a larger system
- Full process development

Plant B (25gpm) – Metals Removal, 4 Hr HRT



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Pre-commercial Scale Demonstration

- At a Refinery Facility in Colorado
- 5-15 gpm (27-84 m^3/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 m^3/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?