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Zero-Valent Iron for Groundwater Remediation – Lessons Learned over 20 years of Technology Use

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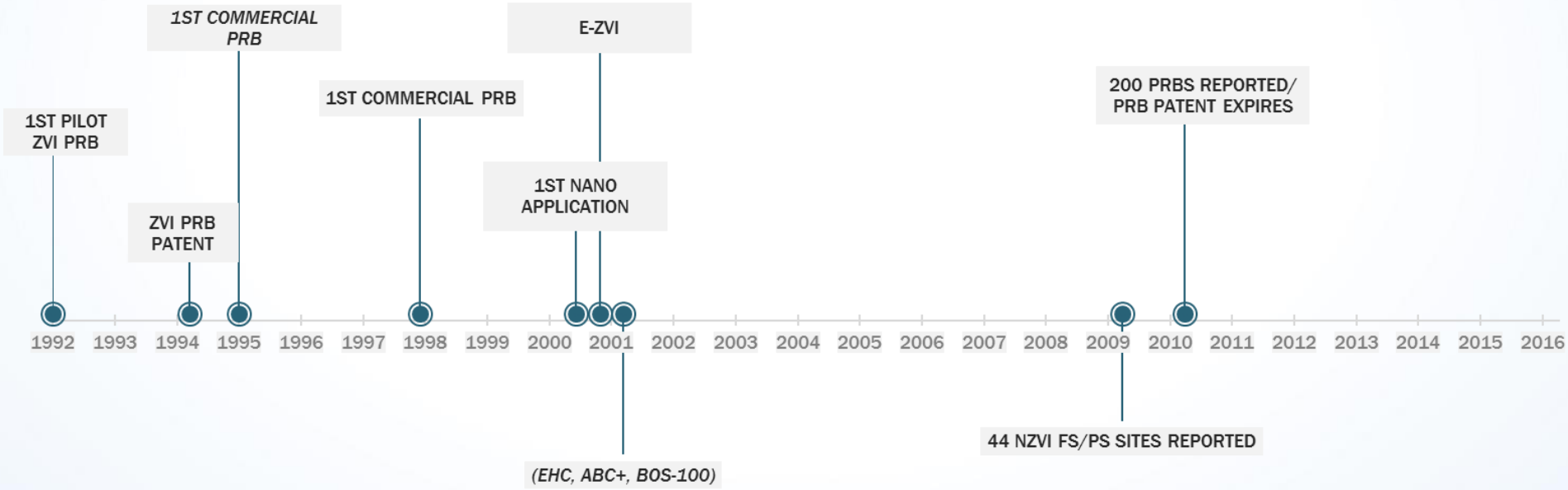
ZVI-Based Remediation Milestones



- Extensive technical information (1,400 technical papers [IronRef], ITRC PRB documents, government and industry reports).
- Commercial vendors of various types of (tested) ZVI media.
- Network of experienced contractors (North America, especially for challenging site conditions; e.g., large depths, bedrock).

Compounds Treated by ZVI

Ethenes:

PCE; TCE;
1,2-DCE isomers; 1,1-DCE; VC

Methanes*:

CT; TCM (CF); TBM

Ethanes*:

1,1,2,2-TeCA; 1,1,1,2-TeCA;
1,1,2-TCA; 1,1,1-TCA;
1,1-DCA

Propanes:

1,2,3-TCP; 1,2-DCP

Other Halogenated:

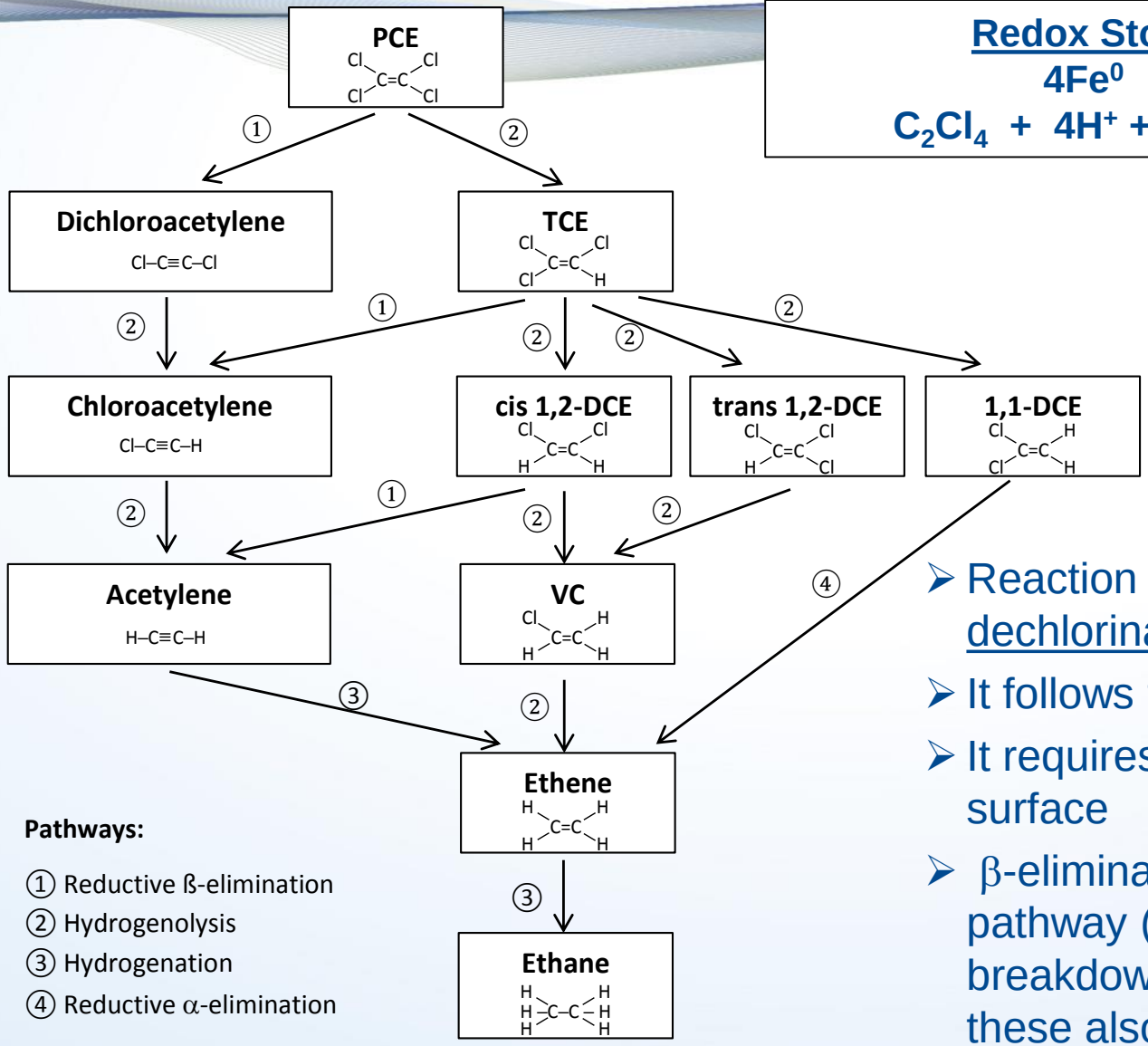
NDMA; DBCP; Lindane;
CFC-113; CFC-11; 1,2-EDB;
DDT

Redox-active Metal(loid)s:

Cr(VI); As(III,V), U(VI), Se(IV,VI)

** 1,2-DCA, CA, DCM, CM not treated by ZVI alone*

cVOC Dechlorination Pathways with ZVI



Redox Stoichiometry (PCE):

$4Fe^0 \rightarrow 4Fe^{2+} + 8e^-$

$C_2Cl_4 + 4H^+ + 8e^- \rightarrow C_2H_4 + 4Cl^-$

- Reaction is abiotic reductive dechlorination
- It follows first-order kinetics
- It requires direct contact with ZVI surface
- β-elimination is the prominent pathway (>90%), therefore breakdown formation is minimal and these also degrade

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Types of ZVI Media and Their Applications

Commercial ZVI Media in Remedial Applications

Scale	Size Range	SSA (m^2/g)	Applications
Millimeter	0.1mm - 2mm	1 - 2	Trenched PRBs, Soil Mixing
Micrometer	20μm - 200μm 1μm - 20μm	3 - 5	Direct injections, Soil Mixing
Nanometer	20nm - 200nm	1 - 58	Direct injections, Injection Wells

SSA –specific surface area

Millimeter

Micrometer

Colloidal

Installation Methods:
Millimeter-Scale

backhoe trenching
(20 ft, 6 m)

biopolymer trenching
(70 ft, 21 m)

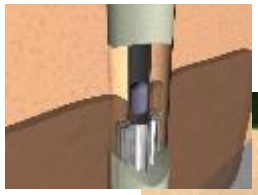
continuous trenching
(35 ft, 11 m)

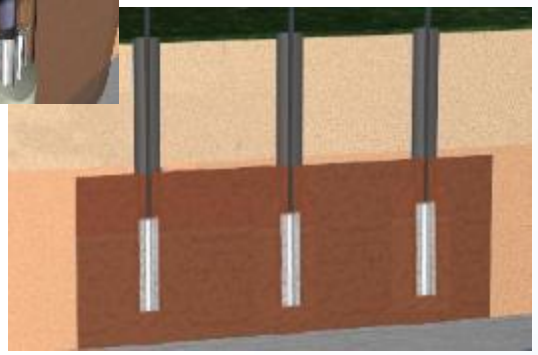
Cofferdam/trench box
(30 ft, 9 m)

Installation Methods:
Micro-, Nano-Scale

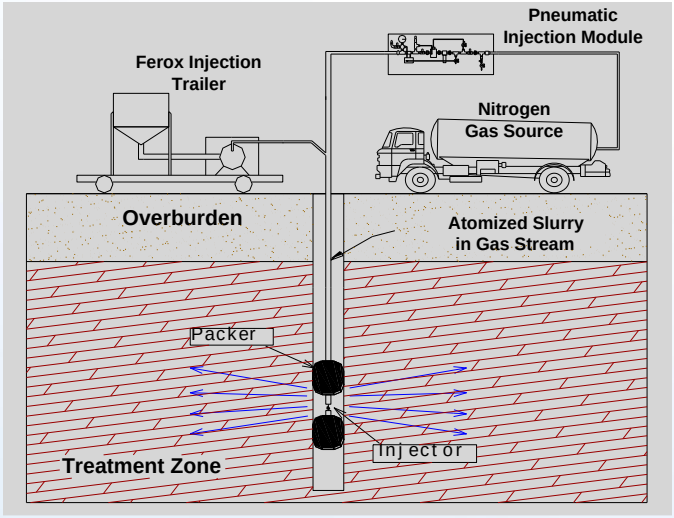
Direct injection
(30 ft, 9 m)

jetting techniques
(60 ft, 18 m)





hydraulic fracturing/injection
(120 ft, 37 m)



Pneumatic
fracturing
(90 ft, 27 m)

In-well applications (Nano)

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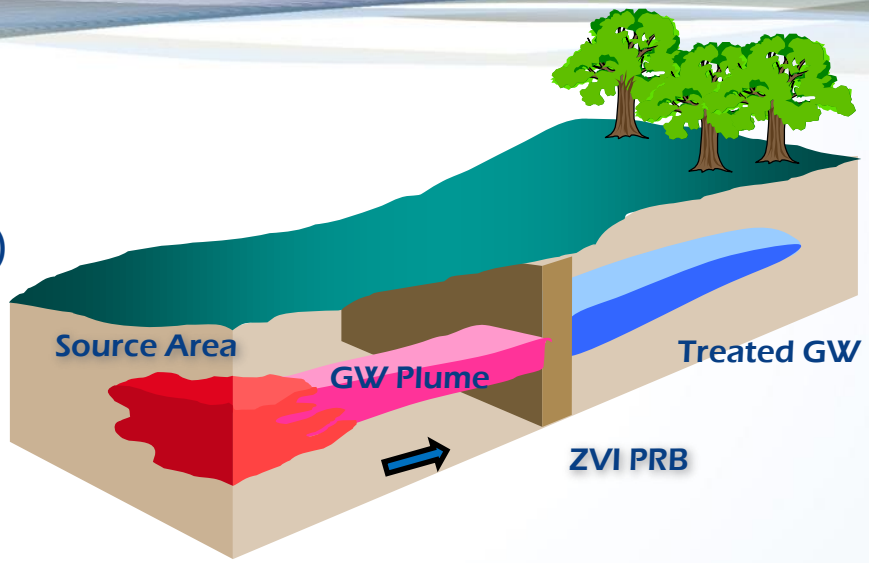
ZVI System Design

ZVI Permeable Reactive Barrier (PRB) Design

Width (W) of PRB

Depends on groundwater velocity (V_{PRB}) and required residence time (RT) of contaminant in barrier

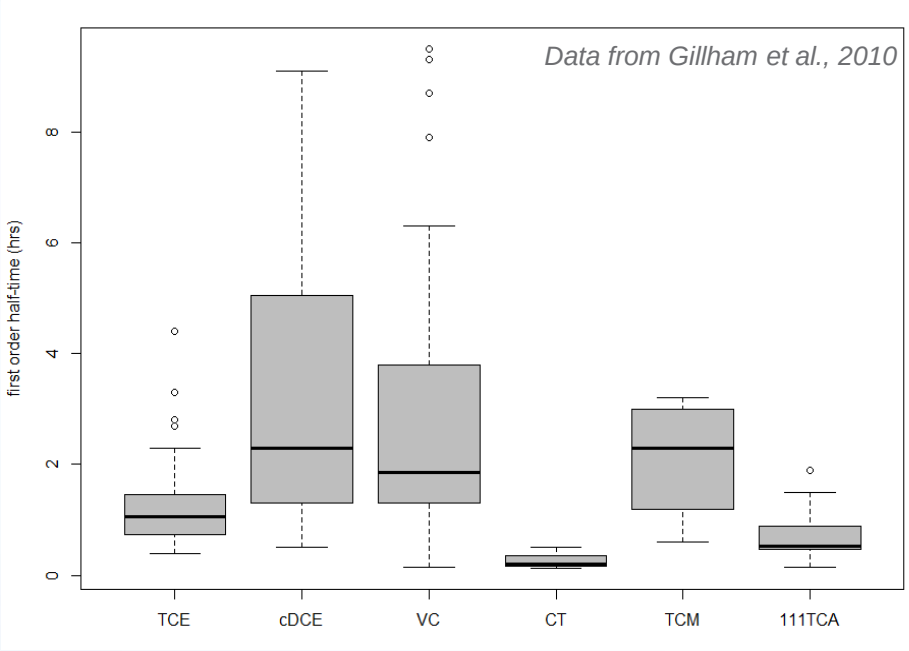
$W = (V_{PRB}) \times (RT)$



Design Residence Time Considerations:

- Initial kinetic rates of degradation in site water.
- Long-term performance effects:
  - Reactivity loss with time.
  - Permeability loss with time.

Variability in ZVI Reactivity



- *Column tests with site groundwaters (same procedure, room temperature).*
- *Two types of commercial milli-ZVIs ("iron filings" Connelly and Peerless).*
- *Total cVOC<30 mg/L, "Typical" chemistries.*

- Critical step in the ZVI PRB design process;
- Use impacted site groundwater in a 2-month long flow-through test;
- Obtain site-specific degradation rates; and
- Indication of rate of passivation/potential fouling.

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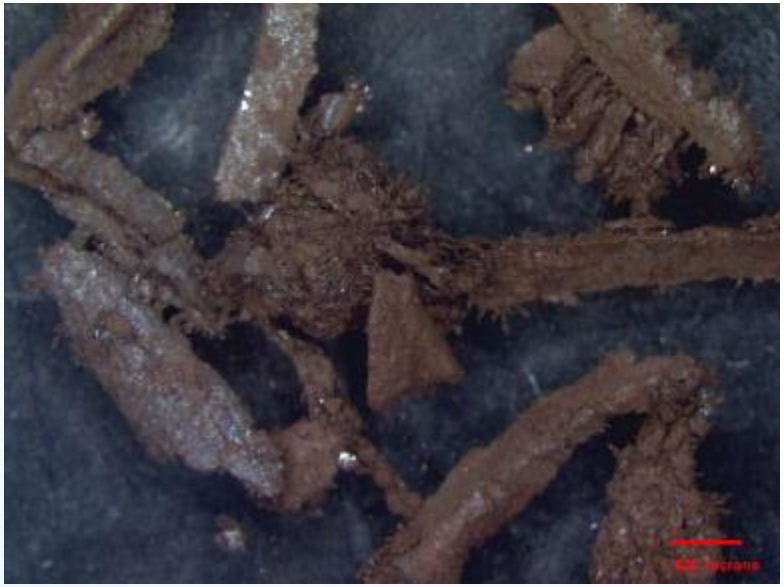
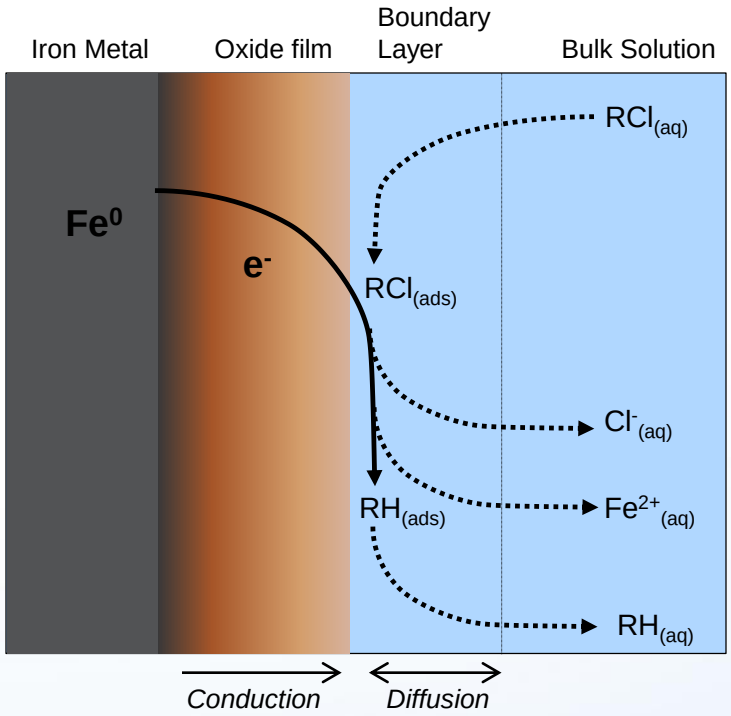
Factors Controlling ZVI PRB Performance

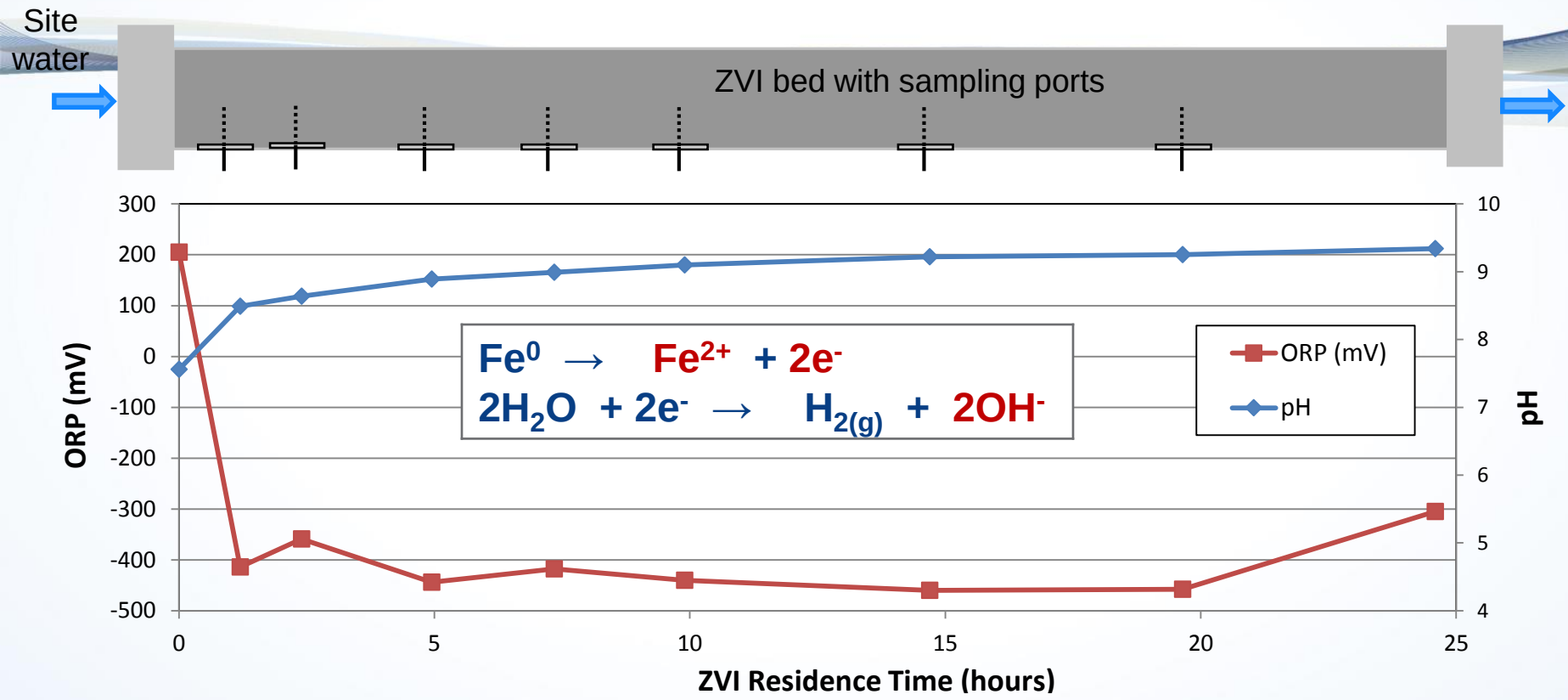
Direct Dechlorination Reactions





Adapted from Tratnyek et al., 2003

Surface Passivation – secondary precipitates



Surface passivation – secondary precipitates:

- High pH effect: Carbonates, iron hydroxides.
- Low ORP effect: iron oxides/oxyhydroxides from ZVI consumption by e^- acceptors: O_2 , NO_3^-, cVOCs, SO_4^{2-} (FeS-microbial).
- Passivating coatings on ZVI grains, e.g.; silica films, organic carbon coatings.

Why ZVI Remedial Systems May Fail

Main reasons why a ZVI PRB may not meet remedial objective:

- Design does not account for a long-term decrease in ZVI reactivity due to interactions with groundwater constituents.
- ZVI is applied in prohibitive geochemical conditions.
- Construction method causes immediate changes to ZVI reactivity and/or permeability.

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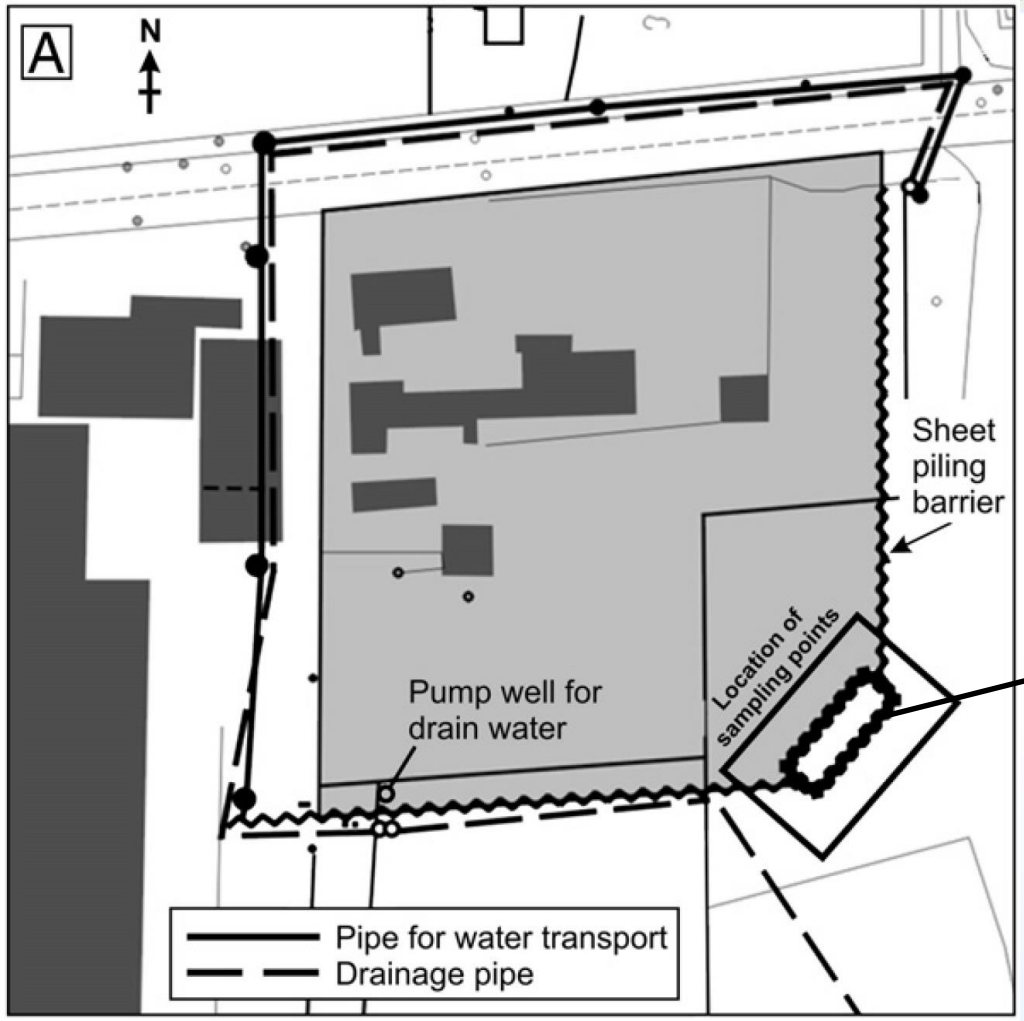
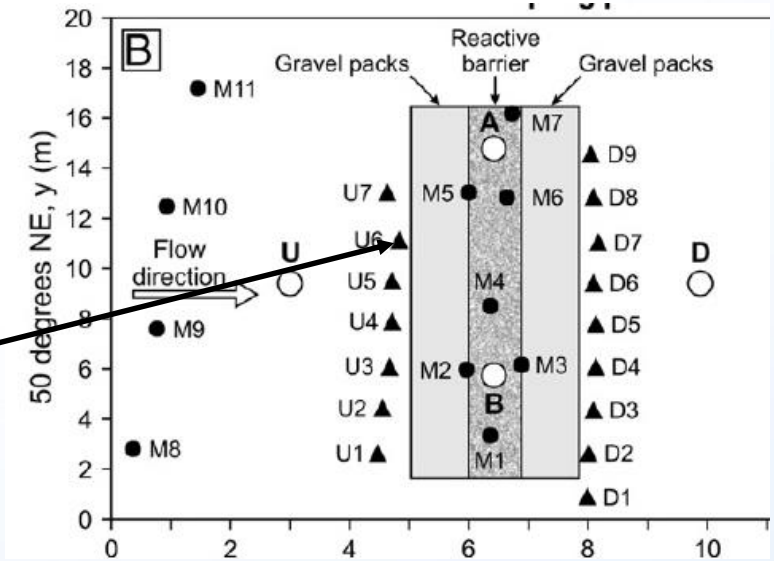
ZVI PRB Performance: Long-Term Inorganic Chemistry Effects

ZVI PRB Case 1



	Conc. mg/L
Ca	190
Mg	73
Alkalinity	440
NO3	0.1
SO4	170

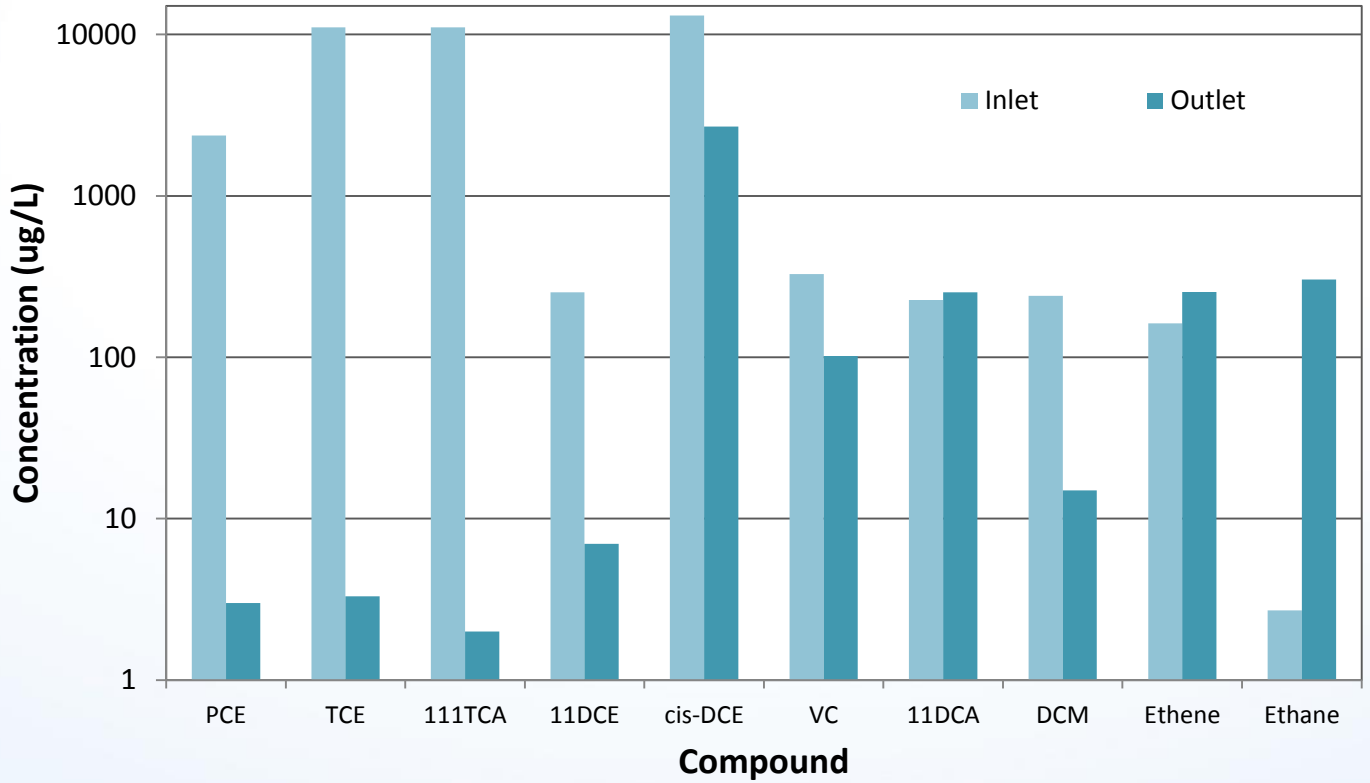


110-130 m funnels, ZVI Gate: L=15 m, D=9 m , W=0.8 m), Gravel (1 m thick) on each side of the ZVI zone

From: Muchitsch et al., 2011

ZVI PRB Case 1

cVOC removal in PRB (8 yrs after construction)



From: Muchitsch et al., 2011

ZVI PRB Case 1
Carbonate Mineral Precipitation

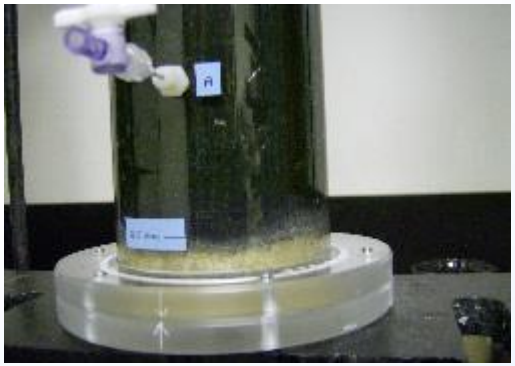
$Fe^0 + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^-$ (pH ~ 9 – 10)
$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O$

Aragonite/Calcite: $Ca^{2+} + CO_3^{2-} \rightarrow CaCO_{3(s)}$
Siderite: $Fe^{2+} + CO_3^{2-} \rightarrow FeCO_{3(s)}$
$2Fe_3O_4 + H_2O + 2H_2 + 3CO_2 \rightarrow 3Fe_2(OH)_2CO_{3(s)}$

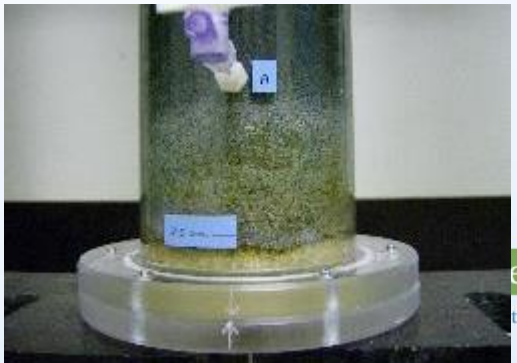
	Conc. mg/L
Ca	190
Mg	73
Alkalinity	440
NO3	0.1
SO4	170

(SEM Image, Jeen et al. 2007)

0 days



52 days



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ZVI PRB Performance: Effects of Prohibitive Constituents

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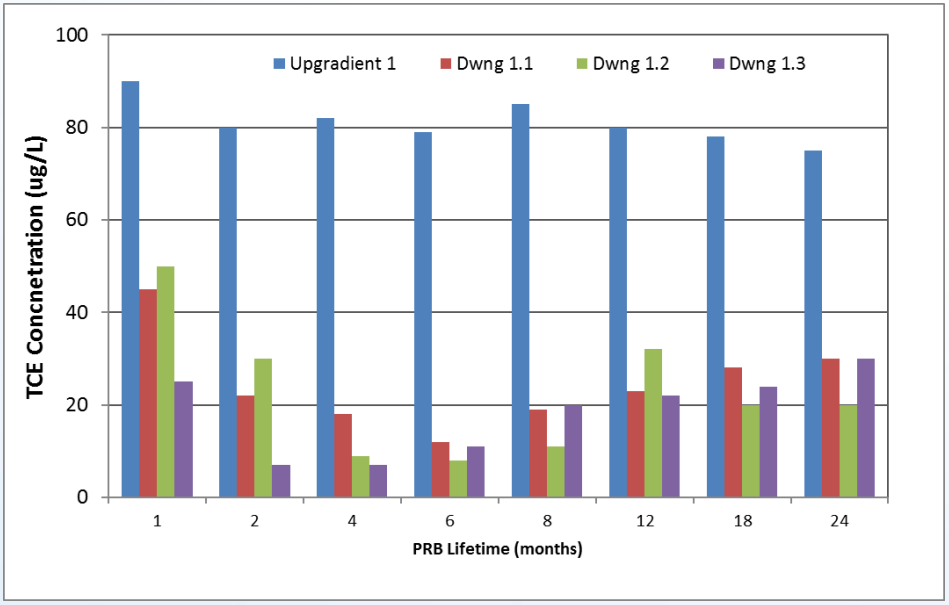
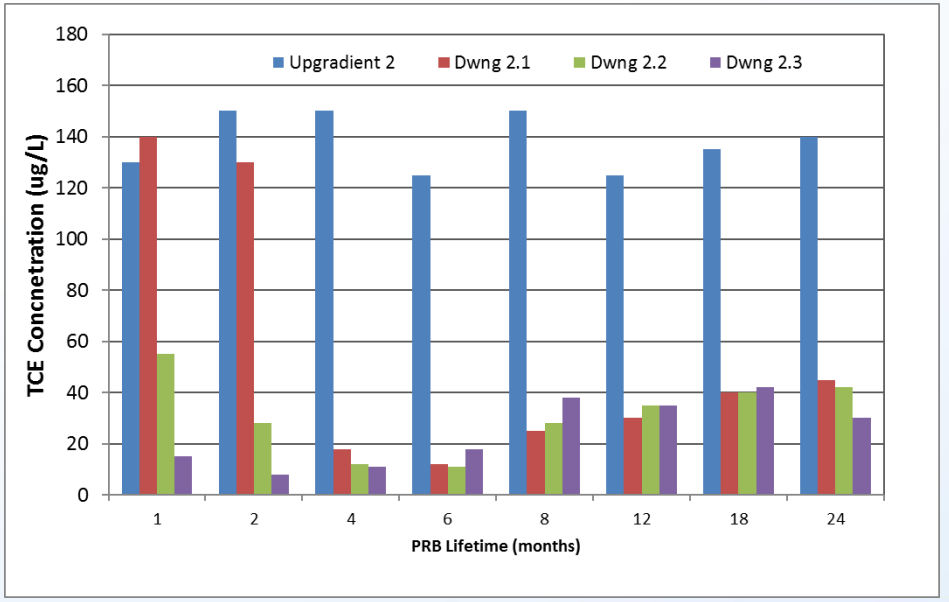
ZVI PRB Case 2
Adverse Nitrate Effect

- Continuous ZVI PRB: 220 m long, 11 m deep.
- Contains 25%wt of ZVI mixed with sand, 0.6 m wide.
- Residence time 1 day.
- TCE concentrations up to 200 µg/L.

	Conc. mg/L
Ca	50
Mg	73
Alkalinity	400
NO_3	6 - 13
SO_4	55

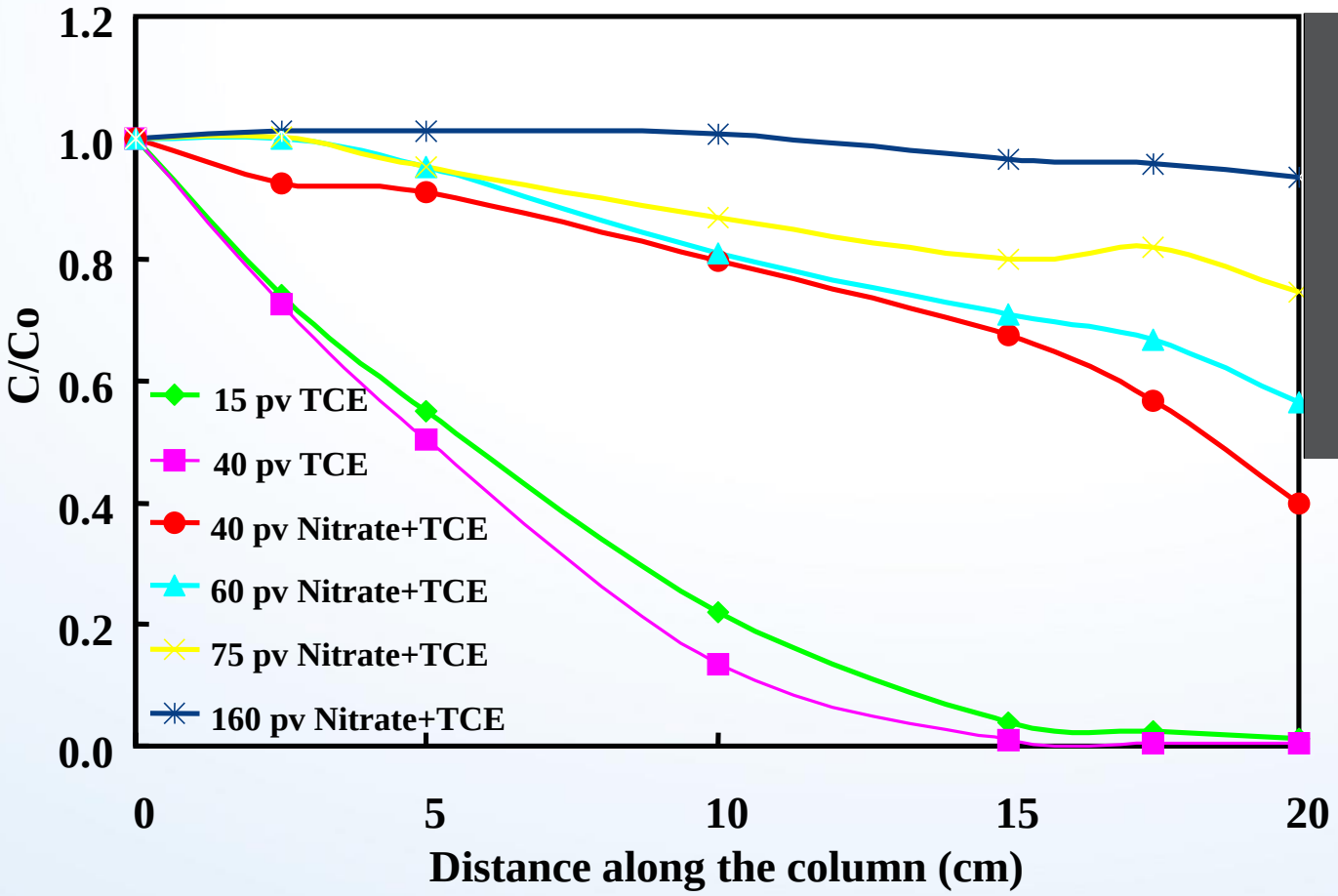


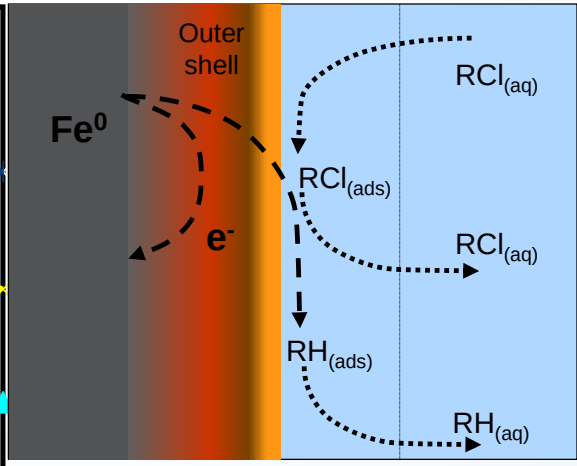


Nitrate Effect

Column Influent 10 mg/L TCE, 47 mg/L NO_3^-

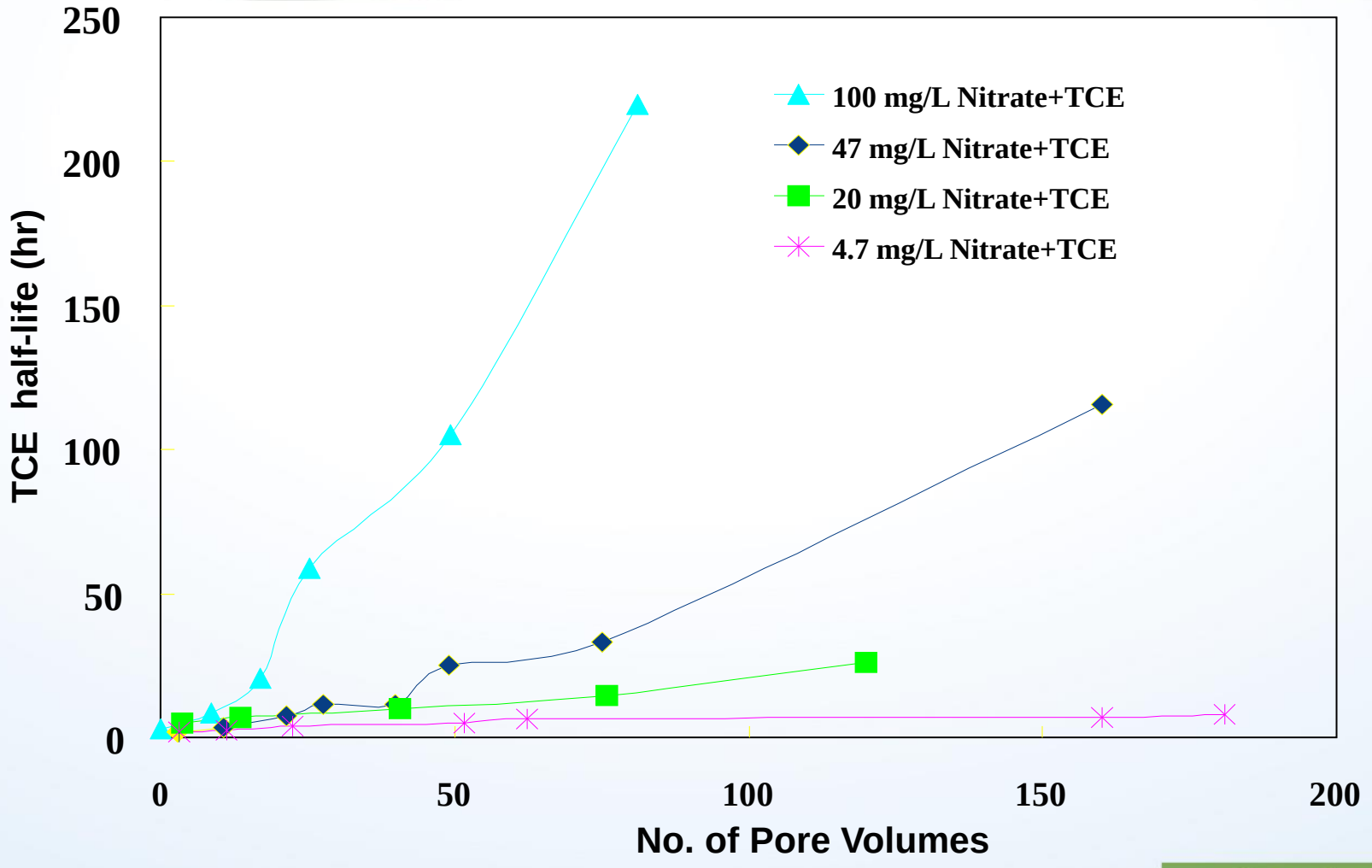
$$NO_3^- + 9\,H^+ + 4Fe^0 \rightarrow NH_3 + 3H_2O + 4Fe^{2+}$$





From Lu, 2005

Changes in half-life of TCE vs. PV



From Lu, 2005

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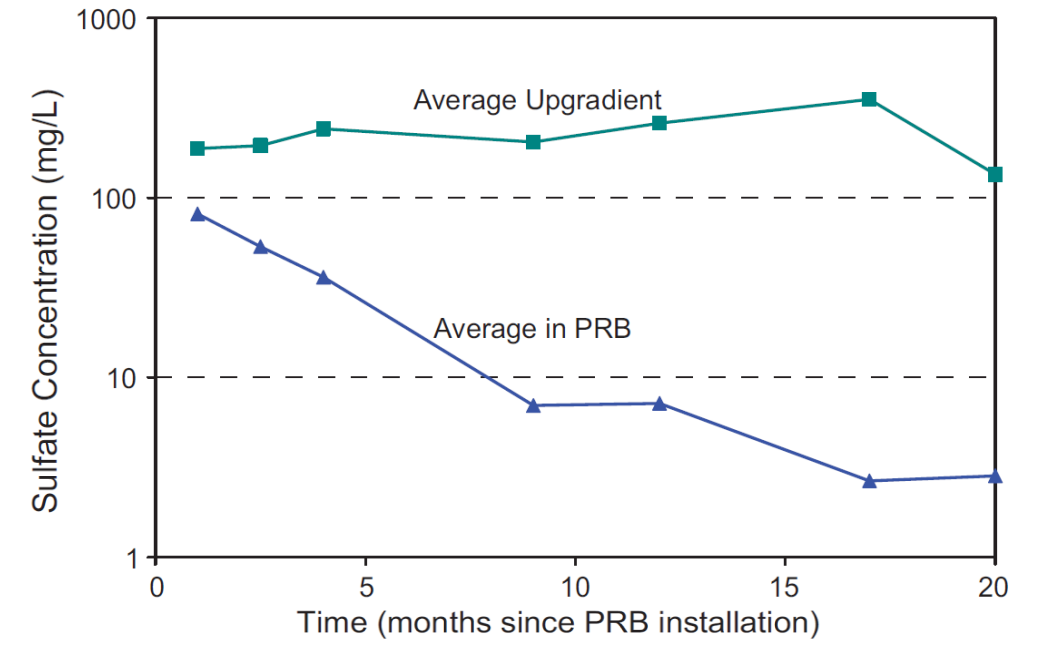
ZVI PRB Performance: Construction Artifacts

ZVI PRB Case 3

- Continuous PRB: 15 m long, 4.5 m deep, 0.9 m wide
- Contains 30%wt of ZVI mixed with sand
- Installed using biopolymer (guar gum) slurry supported excavation.
- TNT concentrations up to 300 µg/L

	Conc. mg/L
Ca	41-175
Mg	12-20
Alkalinity	300-800
NO_3	0-12
SO_4	130-410

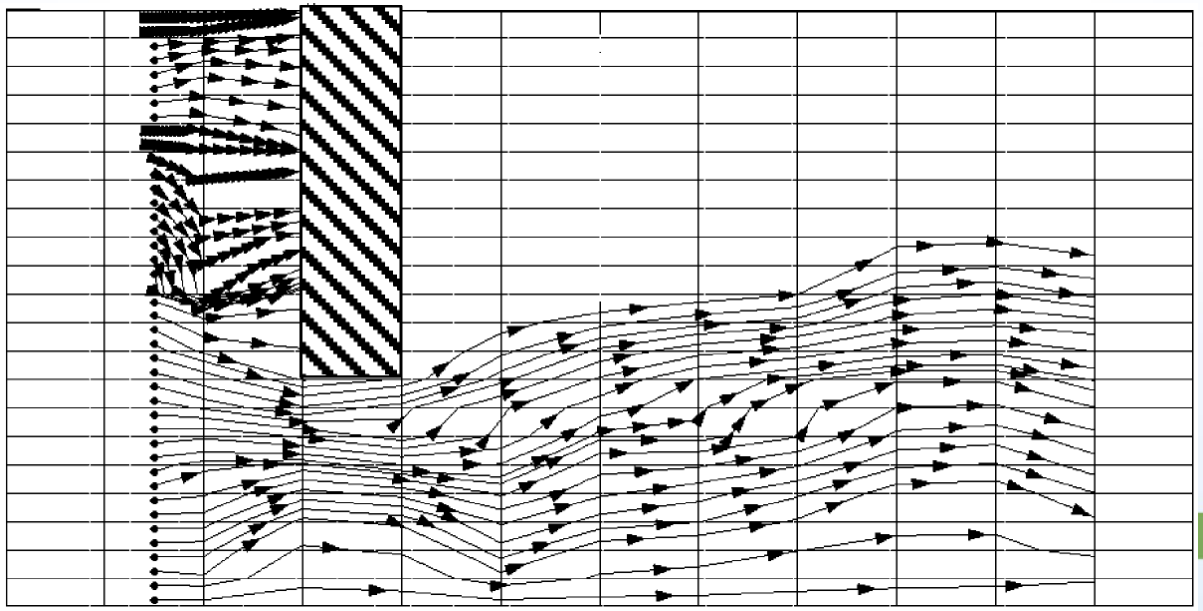


Johnson et al., 2008

ZVI PRB Case 3
Sulfide Precipitation and PRB Plugging

Elevation (bgs)	Sulfate (mg/L) 8	10	11	12	14	16	18
-5.7	80	3	3	3	4	1	1
-6.3	96	2	4	1	15	5	11
-6.9	146	5	1	33	34	29	21
-7.5	161	2	1	28	117	79	139
-8.1	129	1	3	1	270	164	158
-8.7	199	4	20	172	170	181	180
-9.3	260	4	213	262	332	376	355
-9.9	343	285	338	329	311	335	352

$$SO_4^{2-} + 9H^+ + 8e^- \rightarrow HS^- + 4H_2O \Rightarrow Fe^{2+} + HS^- \rightarrow FeS_{(s)} + H^+$$



Johnson et al., 2008

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Summary

Longevity of ZVI-Based Systems

From ITRC, 2011:

Reactive Media	General Range in Longevity
ZVI – Coarse (300 -2,400 µm)	**>15 years**
ZVI – fine/micro (<300 µm)	**5 to more than 10 years**

Many design variables influence the effective life time of ZVI systems :

- Representative field parameters in design (GW velocity, VOC conc.).
- Representative ZVI degradation rates (depend on type of ZVI, type and concentration of VOCs, water chemistry).
- Recognition of prohibitive site conditions (e.g., high concentrations of NO_3^-, or TOC).
- Conservatism in the design to account for gradual passivation of ZVI (depends on mass fluxes of the passivating constituents).
- Proper installation, uniform distribution of ZVI along the GW flow path, no adverse construction effects.