Zero-Valent Iron Reactivity Testing and Project Design

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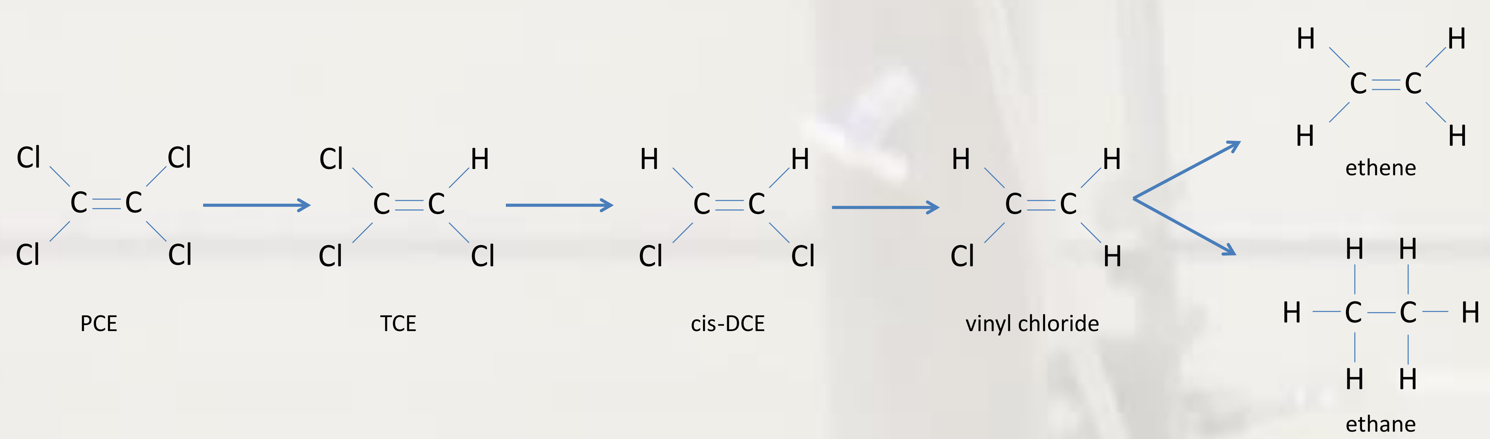
ABSTRACT

Zero Valent Iron (ZVI) is a common remediation option for chlorinated ethenes. Applications now include innovative approaches such as injection of ZVI into the plume or source area and application in the bottom of an excavation, as well as traditional permeable reactive barriers. Combining laboratory-generated reactivity data with simple groundwater flow models can help determine design parameters such as the required reactivity of the ZVI, mass loading, and how geochemistry will effect ZVI performance. However, proper planning, design, and implementation of laboratory tests are critical to obtaining meaningful results. By understanding their options, project managers can better communicate with their laboratories to develop and conduct a successful test, which in turn will help them design applications which are cost effective and meet remediation goals.

ZVI Basics

Zero-valent iron is an established technology for the reduction of chlorinated ethenes (PCE, TCE, DCE, and vinyl chloride). Reactions generally proceed via stepwise reductive dehalogenation with ethene and ethane as the predominant end products (**Eqn. 1**).



Eqn. 1

Transformation of chlorinated ethenes follows pseudo-first order kinetics. If the chemical of concern (COC) is a parent compound (e.g., PCE, or TCE in the absence of PCE), then the COC concentration is given by **Eqn 2a**, which can be rewritten as **Eqn 2b** where *[C]* is the COC concentration at time, *t*; $[C]_0$ is the concentration at time 0; and k_{obs} is the observed pseudo-first order rate constant. A plot of $\ln[C]/[C]_0$ versus time yields k_{obs}, which can be used to size a permeable reactive barrier or determine the amount of iron to inject into a plume. k_{obs} may be normalized to the amount of ZVI used (k_m) by dividing by the concentration of ZVI (Eqn. 2c), so that units of k_m are Vol•mass^{-1}time^{-1}.

$$[C] = [C]_0 e^{-k_{obs}t} \quad \text{Eqn. 2a}$$

$$\ln\frac{[C]}{[C]_0} = -k_{obs}t \quad \text{Eqn. 2b}$$

$$k_m = k_{obs}[ZVI] \quad \text{Eqn. 2c}$$

If a reactive intermediate is produced (e.g. cis-DCE when TCE is the parent compound) then the concentration of the intermediate is given by **Eqn. 3**, where *[I]* is the concentration of the intermediate, α is the fraction of the parent compound converted to the intermediate, kobsP is the pseudo-first order rate constant of the parent compound, and k_{obsI} is the pseudo-first order rate constant for the intermediate. Given the initial concentrations of P and I, k_{obsP} and [I] for several time points, the **Eqn. 3** can be fit to obtain k_{obsI} and α.

$$\frac{d[I]}{dt} = \alpha k_{obsP}[P] - k_{obsI}[I] \quad \text{Eqn. 3a}$$

$$[I] = \left([I]_o + \frac{\alpha k_{obs,P}[P]_o}{k_{obs,P} - k_{obs,I}}\right)e^{-k_{obs,I}t} - \left(\frac{\alpha k_{obs,P}[P]_o}{k_{obs,P} - k_{obs,I}}\right)e^{-k_{obs,P}t} \quad \text{Eqn. 3b}$$

LABORATORY Test Design

ZVI may be evaluated in batch or column tests. Batch tests are usually simpler, quicker, and less inexpensive than column tests, but column tests more closely approximate field conditions.

Batch Tests. Batch tests are most suited to screening candidate ZVI sources for a given site or evaluating the potential for ZVI to treat a specific COC, especially one for which ZVI is not an established remediation option. Batch tests may be conducted in serum vials (**Figure 1a**) or VOAs if the only parameter to be evaluated is VOCs. If other parameters are also of interest, then larger vessels are required (**Figure 1b**.) A good batch test design should

- use site groundwater
- have appropriate controls
- at a minimum, measure DO, ORP, pH in addition to COCs to ensure reducing conditions have been established
- measure chloride to confirm COC destruction increase in chloride due to COC dechlorination would be large enough to detect.

Figure 1a. Batch Tests – Serum Vials.

Figure 1b. 250 mL Reactors.

Column Tests. Multi-port columns consist of influent and effluent ports as well as ports within the ZVI bed. They may be used to assess ZVI only or mixtures of ZVI and sand (**Figure 2**). Rate constants are obtained by collecting samples from each port and plotting the data per Eqns 2 or 3. By measuring rate constants over time (e.g. after 25 pore volumes and after 50 pore volumes have been put through), the effect of aging, if any, on the ability of ZVI to transform COCs can be assessed. A good column test design should

- use site groundwater
- store influent water in such a way as to minimize loss of volatile compounds or changes in DO and other parameters over the course of the test
- measure DO, ORP, pH in addition to COCs to ensure reducing conditions have been established; measurement of ferrous iron is also recommended
- measure chloride to confirm COC destruction if the increase in chloride due to COC dechlorination would be large enough to detect
- measure ethene and ethane to confirm COC destruction
- collect samples in such a way as to minimize loss of volatile compounds or changes in exposure to oxygen
- enable adjustment of flowrate in a timely manner if COCs are not detected in any port except influent. (accurate rate constants can not be calculated if COCs are not detected).
- Minimize the time required to obtain samples. (The more water required for sample analysis, the more time is required to collect the samples. If larger volumes must be collected, larger columns may be advantageous).

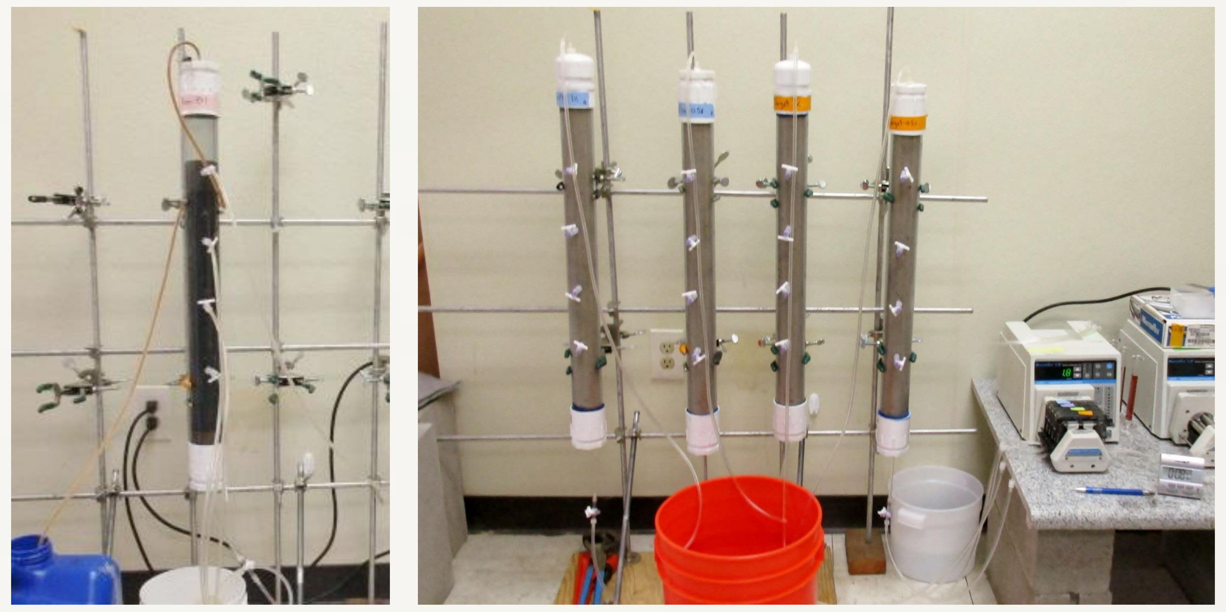


Figure a. Multiport Columns: *Left*: ZVI Only; *Right*: ZVI+Sand

USING Laboratory Data

The mass of ZVI needed to achieve remediation goals can be derived from **Eqn 2b**. Substituting **Eqn 2c** for k_{obs} and expressing *t* as $\varepsilon V/Q$, **Eqn 2b** becomes **Eqn. 4**, where ε is the void fraction, *V* is the "reactor" volume, and *Q* is the flowrate (volume/time). The term $\rho_m \varepsilon V$ is the mass (M_{ZVI}) of ZVI that groundwater will encounter as it passes through a ZVI barrier. Q may be expressed as μnA, where μ is the groundwater flowrate (distance/time), n is porosity, and A is the cross-sectional area of the plume. Substituting these terms into **Eqn 4** and rearranging yields **Eqn. 5**, the mass of ZVI required. If the ZVI is to be applied as a permeable reactive barrier consisting only of ZVI, then the width (Z) of the barrier is given by **Eqn 6**, where ρ_{bulk} is the bulk density of the ZVI.

$$\ln\frac{C_0}{C} = k_m \rho_m \varepsilon \frac{V}{Q} \quad \text{Eqn. 4}$$

$$M_{ZVI} = \frac{\mu nA}{k_m}\ln\left(\frac{C_0}{C}\right) \quad \text{Eqn. 5}$$

$$Z = \frac{M_{ZVI}}{A\rho_{bulk}} \quad \text{Eqn. 6}$$

Pilot Test Design – Barrier versus Plume Treatment

- PCE Plume – 1,000 mg/L
- Clean-up goal – 5 mg/L
- Plume cross-sectional area – 50 ft x 10 ft
- Porosity – 0.33
- Groundwater flow – 0.26 to 0.50 ft/hr
- k_m – 0.00416 ft^3(lb•hr)

ZVI Requirement.

Velocity (ft/hr)	Ferox PRB (lb)	ZVI/Sand (%)		
		PRB	3 ft barrier	50 foot plume
0.011	8,100	0	4.0	0.27
0.025	18,400	0	9.0	0.61