A Geochemical Perspective on the Design, Performance, and Enhancement of Iron Walls

Paul G. Tratnyek
Environmental Science and Engineering
Oregon Graduate Institute of Science and Technology
20000 NW Walker Road, Portland, OR 97006

Permeable reactive barriers (PRBs) of zero-valent iron (ZVI) create an in situ environment with geochemistry that is complex and variable in both spatial and temporal dimensions. Some of the processes that create this environment are specific to the chemistry of iron metal, but many are representative of the (bio)geochemistry of ferrous/ferric iron in the environment as a whole. In fact, some evidence suggests that the main effect of ZVI in PRBs is to create and sustain an environment that is rich in highly-reducing, high-surface area iron oxides, and it may be the high reactivity of these authigenic solids that is primarily responsible for contaminant removal.

The question of the role of Fe^{II} relative to that of Fe^0 in ZVI PRBs has become more difficult, and more interesting, as our understanding of these systems has become more sophisticated. Back in 1994 [1], we tried to capture the essential features of this problem in a conceptual model that distinguished between contaminant reduction by Fe^0, Fe^{II}, and H_2 (Fig. 1A). The major weakness of this model was that it did not make explicit the role of iron oxides or other precipitates on the iron metal. Recently [2], we proposed another conceptual model, which attempts to classify the possible roles of iron oxides vis-a-vis the reduction of contaminants by ZVI (Fig. 1B). These oxides can block the surface, allowing reaction only at pits and other defects; they can transmit electrons by acting as conductors or semiconductors; and they can complex iron, thereby creating reactive sites of adsorbed or structural Fe^{II}.

As with Fig. 1A, the conceptual model represented by Fig. 1B does more to highlight (and hopefully clarify) unresolved issues than it does to answer established questions. Addressing the fundamental issues raised by the new model has been the main focus of our recent research on ZVI PRBs. For example, what are the "reactive sites" that are responsible for the site saturation kinetics that have been reported for various contaminants? Simple answers to these questions have been hard to come by, even for highly-controlled model systems. In addition, it is becoming increasingly apparent that the controlling processes vary with several key system variables, including chemical properties of the contaminants, and temporal and spatial changes in "geochemical" conditions. In other words, the balance between the processes distinguished in Figs. 1A and 1B probably changes along the flow path of a ZVI PRB, evolves as the PRB ages, and shifts with the chemical composition of the influent contaminants.

These dynamics represent "higher order" research questions that have only been addressed qualitatively to date. As we learn more, however, the results are likely to have important practical implications. For example, as a treatment zone ages, the accumulation of iron oxides may provide adsorptive surface area that effectively sequesters the products of contaminant reduction even where these products might otherwise be problematic in the effluent of a ZVI PRB. This appears to be the case with nitro aromatics such as TNT, which produce almost stoichiometric amounts of undesirable aromatic amines in batch studies [3], but hardly any

detectable products in column studies [4]. The conditions that make the column systems so much more useful for treating TNT respond dynamically to changes in flow rate and concentrations of influent oxidants. A specific goal of our current research is to develop a model than can describe these changes as a function of space and time.
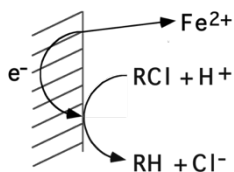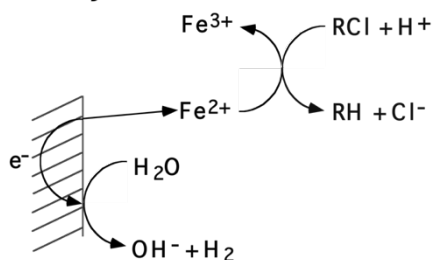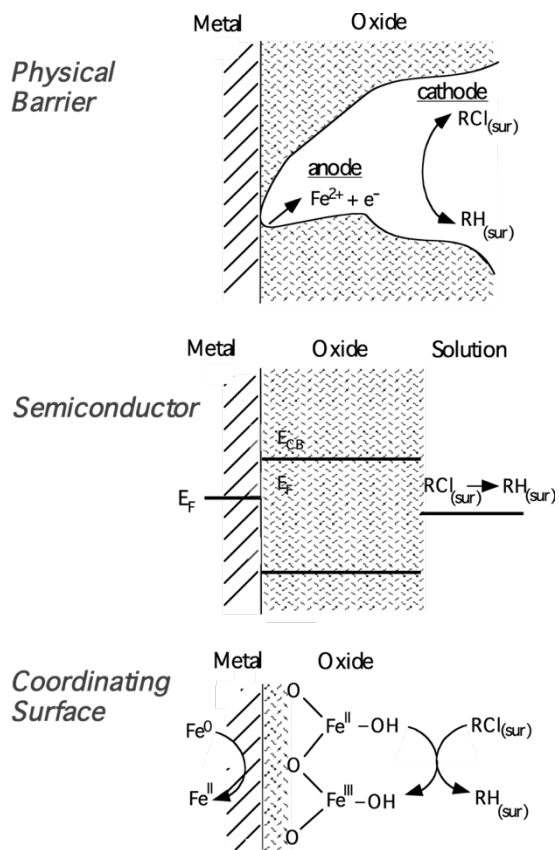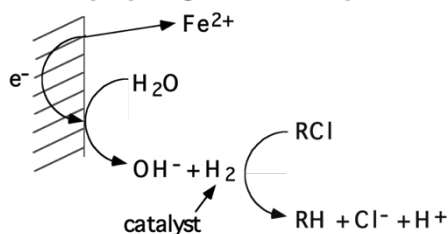

Figure 1. (A) 3 possible pathways for reduction of halogenated aliphatics, RCl, by ZVI. (B) 3 possible roles of the oxide film in reduction of RCl. Adapted from http://cgr.ese.ogi.edu/iron/.

References:
(1) Matheson, L. J.; Tratnyek, P. G. Reductive dehalogenation of chlorinated methanes by iron metal. *Environ. Sci. Technol.* 1994, *28*, 2045-2053.
(2) Scherer, M. M.; Balko, B. A.; Tratnyek, P. G. The role of oxides in reduction reactions at the metal-water interface. In *Mineral-Water Interfacial Reactions: Kinetics and Mechanisms*; Sparks, D. L.; Grundl, T. J., Eds.; American Chemical Society: Washington, DC, 1998; ACS Symp. Ser. 715; pp. 301-322.
(3) Agrawal, A.; Tratnyek, P. G. Reduction of nitro aromatic compounds by zero-valent iron metal. *Environ. Sci. Technol.* 1996, *30*, 153-160.
(4) Johnson, T. L.; Johnson, R. L.; Tratnyek, P. G. Spatial and temporal dynamics in the remediation of TNT by zero-valent iron. in prep.