Published in final edited form as:
Geosci Front. 2023 July ; 14(4): 1–3. doi:10.1016/j.gsf.2023.101583.

Reply to comment on “Long-term performance evaluation of zero-valent iron amended permeable reactive barriers for groundwater remediation–A mechanistic approach” by C. Noubactep, Geoscience Frontiers 14(2023), 101582

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1. Introduction

We welcome the opportunity to address comments provided by Dr. Noubactep and to further emphasize the concepts developed in our article titled “Long–term performance evaluation of zero-valent iron amended permeable reactive barriers for groundwater remediation–A mechanistic approach” (Lawrinenko et al., 2023). The objective of this work was to identify specific hydrological and geochemical factors that impact the long-term performance of zero-valent iron (Fe^0) for treating contaminated groundwater. The selection of groundwater remediation technologies at contaminated sites is best supported by a detailed understanding of site-specific groundwater geochemistry, hydrologic characteristics, and the mechanistic behavior of the treatment technology. Our review is based on decades of field observations and characterization studies at sites with iron-based Permeable Reactive Barriers (PRBs) for treating groundwater contamination. These studies focused on data collection for understanding changes in ground-water chemistry, mineralogical characteristics of the solid-phase, trends in contaminant treatment, and the imprint of subsurface microbiological processes. Dr. Noubactep’s salient comments focus on the following: 1) semantics regarding the use of “reactivity” versus “efficiency.”; 2) his viewpoint that all contaminant remediation in Fe^0 systems is related to the amount of iron corrosion products and their nature because permanent shielding by an electrically non-conducting oxide scale acts as a conduction barrier for electrons and a diffusion barrier for dissolved species; and, 3) his viewpoint that dissolved O_2 is incapable of reacting with zero-valent iron despite being present in groundwater on the influent side of PRBs.

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Declaration of Competing Interest
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Understanding iron corrosion begins at the molecular level. We agree that while the surfaces of Fe^0 particles may not always be in direct contact with groundwater, oxide and oxyhydroxide surfaces formed via corrosion can be in contact with groundwater. Contaminant species can then adsorb to and react on these surfaces. It is important to note that Fe^0 has a cubic, NaCl-type crystal structure. Magnetite (Fe_3O_4), the initial corrosion product, is an inverse-spinel, and subsequent oxides and hydroxides of iron are typically sesquioxides of mostly hexagonal structures characteristic of hydrous ferric oxide ($\sim Fe_5HO_8$ $4H_2O$), hematite (Fe_2O_3), and other iron oxyhydroxides (e.g., goethite, akaganéite). Oxygen can diffuse into corroding Fe^0 particles as described by Shavel et al. (2007) in the form of water and dissolved O_2 and subsequently react with iron. Magnetite initially forms via exsolution due to the change in the chemical environment of iron. Diffusion of Fe^{II} cations into the solid solution of Fe^0 results in a change in volume and a new lattice structure, creating defects. This phenomenon was first described by Smigelskas and Kirkendall (1947) and later investigated by Blin (1954), with more recent research on the formation of hollow nanostructures in alloys by El Mel et al. (2015). The continued development of defect sites and electron transport from internal Fe^0 through semiconducting surfaces provides a long-term source of electrons for reduction reactions.

Numerous SEM micrographs with energy dispersive X-ray analysis of Fe^0 particles collected from field PRBs presented in the literature reveal Fe^0 grains with coatings of corrosion products and other mineral precipitates, especially at the influent side of PRBs where groundwater first comes into contact with Fe^0 grains (e.g., Roh et al., 2000; Furukawa et al., 2002; Phillips et al., 2003). Positions further within the PRB, along the direction of groundwater flow, are characterized by thinner surface coatings, and Fe^0 grains free of surface precipitates near the effluent side of PRBs (Wilkin and Puls, 2003). Often the precipitates coated on the Fe^0 surface block reaction sites, thereby reducing the reactivity of Fe^0 (Roh et al., 2000; Lawrinenko et al., 2023). In extreme cases, cementation of iron oxides, Ca-Fe carbonates, and Fe sulfides results in pore-infilling and the potential for groundwater by-pass around, over, or under PRBs. The most problematic reactants are dissolved oxygen and nitrate (e.g., Liang et al., 2000). Corrosion reactions in which iron reacts to form iron oxides such as magnetite, hematite, goethite, and hydrous ferric oxide result in the formation of low-density products, positive molar volume changes, and porosity reduction. For example, the molar volume change of the reaction (ΔV_r) from Fe^0 to magnetite can be computed from the reaction:

$$Fe^0 + 4/3\ H_2O = 1/3\ Fe_3O_4 + 4/3\ H_2(g) \tag{1}$$

by using the molar volumes (V_m) of Fe^0 and magnetite tabulated in Wilkin and Puls (2003). The molar volume change of reaction (1) is given by:

$$\Delta V_r = 1/3\ (V_m\text{magnetite}) - \left(V_m Fe^0\right) = 6.9\ cm^3/mol \tag{2}$$

Transformation reactions of iron metal to iron hydroxides, oxyhydroxides, and oxides result in positive molar volume changes. Thus, the oxidative transformation of Fe^0 results in pore space reduction; consequently, groundwater containing elevated levels of dissolved oxygen, nitrate, and/or other oxidizing solutes is a concern for the application of technologies that utilize Fe^0 for contaminant treatment (Wilkin and Puls, 2003).

We reviewed other mineralization processes that result in the formation of carbonate, sulfide, and silicate minerals (Lawrinenko et al., 2023). In some cases, these new authigenic precipitates have important beneficial consequences for contaminant removal and transformation. However, other redox processes are required to explain the degradation of chlorinated ethenes, ethanes, dyes, certain metals and metalloids, and metal plating on iron surfaces (e.g., Matheson and Tratnyek, 1994; Cantrell et al., 1995; Fennelly and Roberts, 1998; Arnold and Roberts, 2000; Nam and Tratnyek, 2000; Lawrinenko et al., 2023). Continued electron transport from core Fe^0 through semiconducting surfaces of magnetite promotes the long-term service of Fe^0 in PRBs. This electron transport is responsible for the negative Eh values measured within and down-gradient of ZVI PRBs as reported throughout the literature, and the reduction of contaminants below the +0.77 V reduction potential of Fe^{II} from Fe^{III} (Lawrinenko et al., 2023). While reducing surfaces can be quenched by non-conducting surfaces, if electron transport ceases because of complete encapsulation of the ZVI particle, then there could be no long-term service of Fe^0 in the PRB. The fact that Fe^0 in PRBs does provide years of service in anaerobic groundwater contradicts the concept that particles of Fe^0 are completely encapsulated and electrically insulated from their environment; in addition, encapsulation is contrary to field observation using microscopy analysis. Complete mineralization and encapsulation would render Fe^0 inert after a short period.

Dr. Noubactep’s arguments illustrate the view that corrosion products shield Fe^0 surfaces, and act as a physical barrier to dissolved species. This opinion emphasizes the phenomenon of surface passivation, which can eventually occur; however, such arguments do not provide an explanation for sustained reducing conditions (negative Eh values) and the formation of H_2 under anaerobic conditions within zero-valent iron PRBs. In addition to iron corrosion products, other authigenic mineral precipitates contribute to surface passivation and pore occlusion; namely, sulfides, carbonates, and silicate precipitates (Roh et al., 2000; Lawrinenko et al., 2023). Sulfide minerals such as mackinawite and green rusts that form within PRBs also participate in redox reactions to mitigate contaminants. We agree that the nature and amount of accumulated corrosion product influences overall PRB performance because it affects the reactivity of Fe^0 particles, remediation performance, hydraulic performance, and the transport of contaminants as groundwater passes through a PRB. Corrosion products and other authigenic minerals impact the performance of Fe^0 PRBs and the efficiency of these systems because they influence overall reactivity of Fe^0. However, we question how replacing “the reactivity of Fe^0” by “the efficiency of the Fe^0/H_2O system” would clarify the root of misunderstandings or help improve environmental restoration. Field studies report on achieving remediation goals, and as we discussed in our review, there is a need to better characterize Fe^0 because composition, grain size, material source, crystallinity, and the groundwater geochemical environment all influence the properties of “reactivity”. Furthermore, there exists a need for improved hydrologic models and more field-based studies to improve the design of future PRB installations. We concur with Dr. Noubactep that there is a need for more reliable characterization tools for Fe^0 intrinsic reactivity, which would support the design of sustainable PRBs for groundwater remediation, and we support field data collection efforts that yield practical understanding from real environmental conditions as compared to theoretical exercises and disconnected benchtop investigations. We would also add that there is a need for affordable reactive materials to provide lower cost options for economically disenfranchised communities. Further, recent studies (Lawrinenko et al., 2017; Zhao et al., 2020) have provided greener methods of producing Fe^0 with lower carbon-footprint and have shown that Fe^0 for environmental remediation can be produced through waste diversion and utilization of agroforestry waste materials and iron oxides.

We close by reinforcing our findings that PRBs can be an effective intervention in the remediation of contaminated groundwater. Remediation is a concerted balance of biological, chemical, and physical mechanisms, and a holistic approach is needed to understand mechanisms that occur in the field. Groundwater geochemistry influences PRB performance and mineral precipitation processes within Fe^0 systems. Mineral deposits influence the reactivity of Fe^0; their occurrence also contributes to the overall physicochemical changes in a PRB, affecting groundwater flow and contaminant transport and fate. Additionally, groundwater chemistry also influences subsurface biological processes. Hence, there is a need for continued improvement in characterizing groundwater flow and the transport and fate of contaminants in subsurface systems.

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