

Metallic iron for water treatment: Healing a research community

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Abstract

Despite two decades of intensive research on using metallic iron (Fe^0) for environmental remediation and water treatment, basic concerns about their efficiency still prevail. This communication presents the basic idea of the view that challenges the prevailing paradigm on the operating mode of $\text{Fe}^0/\text{H}_2\text{O}$ systems. The alternative paradigm is in tune with the mainstream science on aqueous iron corrosion. Its large scale adoption will enable a scientifically based system design and increase the acceptance of this already proven efficient technology.

Keywords: Adsorption, Co-precipitation, Filtration, Water treatment, Zero-valent iron.

1 Introduction

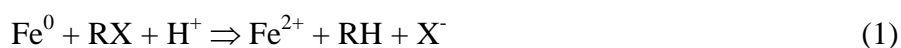
The quest for an affordable (low-cost), applicable (low-maintenance) and efficient technology for water treatment has culminated in the development of metallic iron technology (' Fe^0 technology'). Fe^0 is used both in the subsurface (reactive barriers) and above-ground treatment plants (Noubactep, 2013). Fe^0 has been demonstrated efficient at several sites for the remediation of biological and chemical contamination. However, the operating mode of Fe^0 is still not known (Crane and Scott, 2012; Noubactep, 2012; Noubactep et al., 2012; Togue-Kamga et al., 2012). This frustrating situation is currently endangering the spreading of this proven efficient technology (Mueller et al., 2011; Ruhl et al., 2012a). This communication argues that the major problem of the Fe^0 technology is that scientists are working on an incorrect basis.

2 The original mistake

The Fe⁰ technology was born with the premise that contaminants are reduced as fortuitously observed by Reynolds et al. (1990). From that time on, efforts were directed at identifying the reduction mechanism and the impact of relevant operational parameters thereon (Matheson and Tratnyek, 1994; Ruhl et al., 2012b). Moreover, any likely argument was suggested to justify how electron transfer occurs despite the presence of a (non conductive) diffusion layer (Noubactep, 2011). Any critical view was systematically ignored as presented in details elsewhere (Noubactep, 2011). This attitude has not changed despite the presentation of an alternative concept rationalizing the removal of non reducible species and microbial contamination. As an example, Chen et al. (2012) maintained that “*although there are other mechanisms that likely contribute to organic contaminant removal by Fe⁰ (3 references including Noubactep (2011)), there is substantial evidence from multiple investigators that the abiotic removal of TCE by Fe⁰ largely follows the β-elimination pathway*”. It is interesting to point out that Noubactep (2011) is entitled “*Aqueous contaminant removal by metallic iron: is the paradigm shifting?*” Actually, what is the relevance of the ‘*substantial evidence from multiple investigators*’ if the paradigm is shifting? This example alone evidences that some working researchers on Fe⁰ technology are not willing to test new ideas. Fortunately, some other researchers have positively tested the new concept (e.g. Ghauch et al., 2011; Gheju and Balcu, 2011).

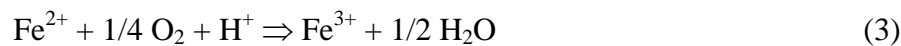
3 The true nature of metallic iron

It is frustrating to notice that equations similar to Eq. 1 are still written to rationalize contaminant reductive transformation.

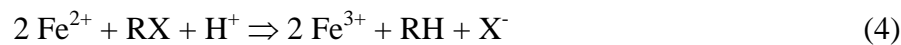


Where RX is a reducible alkyl halide and RH its reduced form. RH is less toxic than RX as a rule. RH is more biodegradable.

From the open literature on iron corrosion however, it is known that Fe^0 is permanently covered by an oxide scale (Stratmann and Müller, 1994; Cole and Marney 2012; Wang et al. 2013). Even dissolved oxygen (O_2) can not quantitatively reach the iron surface such that iron is essentially corrodes by water (H^+ , Eq. 2) and O_2 reduced by Fe^{2+} (Eq. 3) (Stratmann and Müller, 1994).



Disregarding the relative affinity of species of concern to iron oxides, the question arises why a RX , that is necessarily larger in size than O_2 should diffuse through the oxide film. This question suggests that equations like Eq. 4 should be routinely used to model processes in $\text{Fe}^0/\text{H}_2\text{O}$ systems.



Next to Fe^{II} species as relevant reducing agent, future research should properly consider the volumetric expansive nature of iron oxidation in discussing the evolution of the porosity of Fe^0 filtration systems (Caré et al., 2013). It may be difficult to admit, that the volumetric expansive nature of metal corrosion, that was presented 90 years ago (Pilling and Bedworth, 1923; Caré et al., 2008), has not been properly considered in discussing the decrease of the hydraulic conductivity of $\text{Fe}^0/\text{H}_2\text{O}$ systems (Henderson et al., 2011; Ruhl et al., 2012; Jeen et al., 2013). The ongoing discussion considers H_2 and foreign precipitates including CaCO_3 and FeCO_3 (Henderson et al., 2011; Henderson et al., 2013; Jeen et al., 2013) but not properly hydroxides and oxides. Overseeing the importance of volumetric expansion has let to various explanations of the fact that a pure Fe^0 system is not sustainable. The best illustration is perhaps a recent paper by Ruhl et al. (2012b) evaluating the suitability of admixing Fe^0 with anthracite, gravel, pumice and sand in fixed bed filters for TCE removal. The authors concluded that none of the four dual systems was applicable for the remediation of tested groundwater. This conclusion disregards the historical work of O'Hannesin and Gillham

(1998) at Borden, Ontario (Canada) which can be regarded as the cornerstone on which the 'Fe⁰ technology' is built. O'Hannesin and Gillham (1998) demonstrated the efficiency of a 22:78 Fe⁰:sand weight ratio for the removal of TCE (and PCE). The reactive wall in Borden (Canada) was the first full-scale Fe⁰ reactive barrier.

4 Reactivity and efficiency of iron materials

Another important point is that the term 'reactivity' is confusing through the 'Fe⁰ technology' literature. Reactivity is per definition an intrinsic, invariable characteristic, a trend that can not be strictly quantified but can be assessed by standard protocols (if available). For example, the intrinsic reactivity of Fe⁰ can be assessed by the extent of H₂ evolution under controlled conditions. It is essential to notice that the reactivity of a material does not depend on its amount or its proportion in a mixture. Accordingly, if a Fe⁰ material is mixed with an inert sand, its reactivity is not changed but the extent of its dissolution (e.g. coupled to H₂ evolution) is modified as sand can not contribute to H₂ generation nor to porosity loss. In other words, mixing sand and Fe⁰ is a tool to sustain the efficiency of the system (not the reactivity of Fe⁰). Many reported discrepancies can be attributed to the randomly interchanged use of 'reactivity' and 'efficiency' (Miyajima, 2012). To clarify this semantic issue it could be stated that the efficiency is the expression of the reactivity as impacted by operational conditions.

5 Conclusion

The Fe⁰ research community is aware on the instability of the concept that contaminants are removed in Fe⁰/H₂O systems by a reductive transformation (Liu et al. 2013) but is still not really willing to test new ideas. The situation is comparable to that of a person facing a blockade and being aware on it. Furthermore, the person can not recognize the way out of the blockade. Whenever this is the case, a professional assistance is needed: a modern psychologist or a traditional healer? It seems that a healer should intervene to redirect the Fe⁰ research community on the highway of iron corrosion.

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