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Review

Metallic iron for environmental remediation: A review of reviews

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ABSTRACT

This article critically evaluates recent review articles on using metallic iron (Fe^0) for environmental remediation in order to provide insight for more efficient Fe^0-based systems. The presentation is limited to peer-reviewed articles published during 2014 and 2015, excluding own contributions, dealing mostly with granular Fe^0. A literature search was conducted up to June 15th 2015 using *Science Direct*, *SCOPUS*, *Springer* and *Web of Science* databases. The search yielded eight articles that met the final inclusion criteria. The evaluation clearly shows that seven articles provide a narrative description of processes occurring in the Fe^0/H_20 system according to the concept that Fe^0 is a reducing agent. Only one article clearly follows a different path, presenting Fe^0 as a generator of adsorbing (hydroxides, oxides) and reducing (Fe^{II}, H/H_2) agents. The apparent discrepancies between the two schools are identified and extensively discussed based on the chemistry of the Fe^0/H_20 system. The results of this evaluation indicate clearly that research on 'Fe^0 for environmental remediation' is in its infancy. Despite the current paucity of reliable data for the design of efficient Fe^0-based systems, this review demonstrates that sensible progress could be achieved within a short period of time, specific recommendations to help guide future research are suggested.

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1. Background

Granular metallic iron (Fe^0) has been increasingly used as filling material in subsurface artificial permeable reactive barriers (PRBs) for the last 20 years (Phillips et al., 2010; Gheju, 2011; Muchitsch et al., 2011; Wilkin et al., 2014; Statham et al., 2015; Vodyanitskii and Mineev, 2015). Compared to the conventional pump-and-treat technology, the Fe^0 PRB technology is more efficient and significantly less expensive (Higgins and Olson, 2009; Statham et al., 2015; Vodyanitskii and Mineev, 2015). Currently, there are more than 200 Fe^0 PRBs installed around the world (Vodyanitskii, 2014a). These installations have been reported to mostly satisfactorily working. However, their efficiency has been reported to be limited by factors, that are inherent to aqueous iron corrosion.

Guan et al. (2015) summarized the major limitations of Fe^0 PRB technology as follows (see also Bartzas and Komnitsas, 2010; Li and Benson, 2010): (i) low reactivity due to the availability of an oxide scale on Fe^0, (ii) narrow working pH, (iii) permeability loss due to precipitation of metal hydroxides and carbonates, (iv) low selectivity for target contaminants especially under oxic conditions, (v) limited efficacy for treatment of some refractory contaminants and (vi) Fe^0 passivity arising from certain contaminants and/or co-solutes.

Guan et al. (2015) also gave a survey of countermeasures to address the limitations of the Fe^0 technology. These countermeasures are: (i) pre-treating available Fe^0 materials to remove the (passive) oxide scale, (ii) reducing the size of Fe^0 materials down to nano-size to increase the surface area, (iii) manufacturing Fe^0-based bimetals to increase the number of galvanic cells (and thus accelerate Fe^0 oxidation), (iv) using physical methods to free the Fe^0 surface from passive layers, (v) admixing Fe^0 with a proper adsorbent, (vi) chemically enhancing Fe^0 reactivity, and (vii) restoring the reactivity of aged Fe^0.

A survey of the countermeasures to maintain the efficiency of Fe^0 PRBs suggests that conventional PRBs would have not worked as reported. In fact, no named countermeasure has been applied at Elizabeth City (North Carolina) and the Fe^0 PRB has being successfully working for more than fifteen (15) years, treating a groundwater contaminated with chromate and trichloroethylene (TCE) (Wilkin et al., 2014). TCE treatment was not always effective, supposedly due to non-constant influent concentrations. This aspect is not discussed herein. The most important feature is that the installation has been working for more than 15 years. On the other hand, a survey of the limitations of Fe^0 PRBs should lead to the net conclusion that no Fe^0-based system is viable in the long-term for at least two reasons: (i) the Fe^0 surface is constantly shielded by an oxide scale (Cohen, 1959; Stratmann and Müller, 1994; Sato, 2001; Nesic, 2007) meaning the low reactivity is part of the system, and (ii) the pH value of a groundwater cannot be modified prior to treatment with Fe^0 PRBs. In another phrase, it seems that some of the named limitations are the real strengths of the Fe^0 PRB technology. In particular, it is sufficient to regard Fe^0 as a generator of iron oxides (for contaminant removal) (Tseng et al., 1984; James et al., 1992; You et al., 2005; Erickson et al., 2007, 2012) instead of being a curse (inhibiting contaminant reductive transformation) and the oxide scale then becomes a blessing (Ghauch et al., 2011; Gheju and Balcu, 2011; Ghauch, 2015).

1.1. The problem

The concept that Fe^0 is a generator of (i) reducing agents (Fe^{II}, H/H_2) and (ii) removing agents (iron hydroxides and oxides) for contaminant transformation (if applicable) and removal has been introduced in the peer-reviewed literature since 2007 (Noubactep, 2007a, 2008) but has been largely ignored (Fu et al., 2014) or improperly considered (Chen et al., 2013). Two examples will be given for illustration.

Kang and Choi (2009) predicted a hart time to the new concept with the following wording: “Noubactep questioned the premise that Fe^0-induced contaminant removal is initiated by the direct electron transfer from Fe^0 to substrates and added that “the premise was already questioned and/or proven inconsistent” with citing only his own papers (Noubactep, 2007a, 2008). This argument is hardly acceptable since the role of the direct electron transfer in Fe^0-mediated reactions is well established and generally accepted among the research community”.

Later, Tratnyek and Salter (2010) added the following comments: “Noubactep's comment on our paper (Sarathy et al., 2010) is similar to others that he has published recently, including five in this journal (Noubactep, 2007b, 2009a, 2009b, 2009c, 2009d) and at least 10 in other journals. He has also published about six short reviews that make similar arguments, most recently in Noubactep et al. (2012a).

The nonsequiters in Noubactep's contributions are so pervasive that it is difficult to ascertain which parts have merit. This is apparent from the rebuttals to Noubactep's commentaries, where the original authors clearly have struggled to find constructive ways to respond”.

These two comments may suggest that (i) it is not worth the effort of paying any attention to the concept presented by Noubactep and (ii) experimental results are needed to support the new concept.

1.2. Origin of the problem

The controversy on the operating mode of Fe^0-based systems for water treatment originates from the approach used in their investigation. The technology was born at a time where groundwater remediation researchers were looking for suitable materials for PRBs after the concept presented by McMurty and Elton (1985). In fact, Reynolds et al. (1990) were investigating the potential for sampling bias caused by sorption of chlorinated organic contaminants to materials commonly used in groundwater sampling as they discovered ‘halocarbons loss’ due to reductive dechlorination (Gillham, 2010). This reproducible observation was further investigated in the laboratory. Matheson and Tratnyek (1994) presented the first mechanistic investigations. Despite some parallel sceptical views (Lipczynska-Kochany et al., 1994; Warren et al., 1995; Lavine et al., 2001) reductive transformation was consensually adopted (O'Hannesin and Gillham, 1998; Kang and Choi, 2009; Chen et al., 2013), since then, the suitability of Fe^0 for water treatment has been tested on a case-by-case basis and results are tabulated in numerous overview and review articles (Scherer et al., 2000; Richardson and Nicklow, 2002; Henderson and Demond, 2007; Chen et al., 2013). However, this pragmatic research approach