Chicgoua Noubactep*

Metallic iron for environmental remediation: the long walk to evidence

Abstract: The science of metallic iron for environmental remediation is yet to be established. The prevailing theory of the Fe⁰/H₂O system is characterized by its inability to fully rationalize the concept that holds up the technology. The present article demonstrates that Fe⁰ technology was introduced by altering the course of mainstream science and by distorting the work of corrosion scientists. The Fe⁰ research community is now facing the consequences of this initial “forcing”. The technology is still innovative despite two decades of commercialization.

Keywords: corrosion science; environmental remediation; water treatment; zero-valent iron.

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1 Introduction

Metallic iron (Fe⁰, iron metal) is commonly termed “zero-valent iron” within the environmental research community. Fe⁰ is extracted at high temperature from iron ores (mostly oxides). This exothermic operation makes Fe⁰ unstable under atmospheric conditions as the trend back to the more stable oxides cannot be permanently prohibited. This oxidative dissolution process is commonly known as iron corrosion, which is usually mostly a destructive process. However, examples of taking advantage from iron corrosion are also well documented (Noubactep, 2013a) For example, porous direct reduced iron (sponge iron) has been tested as an alternative to compact Fe⁰ material for contaminant removal in passive filters, including Fe⁰ permeable reactive barriers (PRBs) during the past two decades (Ebert et al., 2006; Li, Li, & Li, 2009; Li, Wei, Li, Bi, & Song, 2011; Schlicker et al., 2000; Yi et al., 2013). However, sponge iron is a traditional material used as oxygen scavenger in water treatment plants (Li et al., 2011; Yi et al., 2013).

The use of Fe⁰ for in situ treatment of groundwater was first proposed by Canadian hydrologists approximately two decades ago (Gillham & O’Hannesin, 1992; Reynolds, Hoff, & Gillham, 1990). Initially, Fe⁰ was used as filler for PRBs. Basically, a Fe⁰ PRB consists of a porous diaphragm wall of granular Fe⁰, often mixed with sand or gravel, in which the inflowing contaminated groundwater is treated (Bartzas & Komnitas, 2010; Comba, Di Molfetta, & Sethi, 2011; Crane & Scott, 2012; Gheju, 2011; Li & Benson, 2010; Noubactep, Caré, & Crane, 2012a; Noubactep, Temgoua, & Rahman, 2012b; Phillips et al., 2010). Currently, more than 200 Fe⁰ PRBs have been satisfactorily installed worldwide (Chiu, 2013; Interstate Technology & Regulatory Council, 2011). However, confusing reports on all aspects of the Fe⁰ PRB are still currently reported. For example, a recent research article (Ruhl, Ünal, & Jekel, 2012) disproved the efficiency of dual Fe⁰/material filters to treat groundwater contaminated with trichloroethene (TCE). However, the suitability of Fe⁰ PRBs for environmental remediation was demonstrated earlier using exactly TCE and a Fe⁰:sand weight mixture of 22:78 (O’Hannesin & Gillham, 1998).

The objective of this article is to demonstrate that the frequency of controversial reports originates from the lack of a sound theory of the Fe⁰/H₂O system which in turn originates from an improper consideration of the huge literature on aqueous iron corrosion. The state-of-the-art knowledge on the process of contaminant degradation/removal in Fe⁰/H₂O systems will be given first.

2 Contaminant degradation in Fe⁰/H₂O systems

Using TCE (a halogenated hydrocarbon) as the model contaminant, the prevailing degradation mechanism in Fe⁰/H₂O systems can be summarized as follows (Cai et al., 2013; Zhao & Reardon, 2012): (i) Fe⁰ acts as an electron donor to reductively degrade TCE, (ii) the electron transfer occurs at the Fe⁰/water interface, (iii) the degradation pathways include reductive β-elimination (primary), hydrogenolysis (minor) and catalytic hydrogenation (minor), and (iv) TCE can be degraded directly by Fe²⁺ ion. Fe⁰ and H/H₂ are produced from Fe⁰ corrosion.

For other compounds than TCE, more than one reaction may occur. Moreover, intermediates and/or reaction
products may be more toxic than the parent contaminants. Therefore, the suitability of Fe\(^{0}\) PRBs for relevant contaminants was tested on a case-by-case basis (Chiu, 2013; Richardson & Nicklow, 2002). Thereby, contaminants were grouped based on questionable criteria. For example, individual research groups tested the suitability of Fe\(^{0}\) to remove azo dyes, heavy metals, nutrients, radionuclides and constituents present in agricultural/hospital wastes or pharmaceuticals and personal care products (Cai et al., 2013). However, none of these classes of compounds is homogeneous with regard to chemical nature, structure and reactivity (Komnitas, Zaharaki, Doula, & Kavvadias, 2011; Kümmmerer, 2009; Nödler, Licha, Bester, & Sauter, 2010; Schaffer, Börnick, Nödler, Licha, & Woroch, 2012). It is not likely that these compounds are all sensitive to reduction by Fe\(^{0}\). Even if they were reductively transformed by Fe\(^{0}\), three major issues still need to be addressed: (i) the sustainability of reduction after inherent oxide film formation, (ii) the nature of the reaction products, and (iii) the environmental fate of the reaction products.

3 Reductive transformation: the original sin

The Fe\(^{0}\) PRB technology was born with the serendipitous observation that chlorinated organic contaminants were lost from groundwater sampled in metallic vessels (Gillham & O’Hannesin, 1992; Reynolds et al., 1990). The observed mass loss of chlorinated organic compounds was reproducible and was attributed to reductive dechlorination by Fe\(^{0}\) (Reynolds et al., 1990). This observation coincided with the active search of relevant reactive materials for PRBs after the concept had been presented by McMurty and Elton (1985). From this moment on, Fe\(^{0}\) was considered as a reducing agent (direct reduction). The remaining challenge was to identify the reduction pathway (Hardy & Gillham, 1996; Matheson & Tratnyek, 1994). This goal was considered to be widely achieved with the works of Weber (1996) and Arnold and Roberts (2000).

The experimental observation that chlorinated organic compounds are reductively transformed in the presence of Fe\(^{0}\) or in Fe\(^{0}/\)H\(_2\)O systems could be retrospectively considered as a curse/sin for the development of this technology. In fact, this technology is still based on this apparently unquestionable reductive transformation theory. However, this theory has never been accurately tested and validated by any scientific method, nor has it been univocally accepted (Noubactep, 2011a,b). Accordingly, the current controversy surrounding the reductive transformation theory is not new anymore as shortcomings of the original premise have been repeatedly highlighted (Farrell, Wang, O’Day, & Conklin, 2001; Lavine, Auslander, & Ritter, 2001; Liu, Wang, Wang, & Li, 2013; Odziemkowski, 2009). However, the negation of the still prevailing reductive transformation theory has been exacerbated by the presentation of an alternative theory (Noubactep, 2007).

4 Adsorption/co-precipitation concept

The reductive transformation theory cannot explain why contaminants without redox properties with respect to the Fe\(^{2+}/\)Fe\(^{0}\) couple (e.g., methylene blue, triazoles, Zn\(^{2+}\)) are quantitatively removed in Fe\(^{0}/\)H\(_2\)O systems. Moreover, this theory has not clearly specified the fate of non-reduced parent compounds and reaction products. Evidence, that (i) named compounds are quantitatively removed in Fe\(^{0}/\)H\(_2\)O systems, (ii) chemical reduction is not a standalone mechanism of aqueous contaminant removal, and (iii) corrosion is a volumetric expansive process, has motivated the introduction of a new theory for the system (Noubactep, 2007, 2008, 2010a,b).

The new theory stipulates that contaminants are basically removed by a non-specific mechanism similar to electrocoagulation (Bojic, Bojic, & Andjelkovic, 2009; Noubactep & Schöner, 2010). Accordingly, contaminants are adsorbed and/or sequestered in the matrix of precipitating iron hydroxides, whether they are chemically transformed or not. In column experiments, in situ generated expansive precipitates reduce the pore volume and improve the size exclusion process. In other words, an Fe\(^{0}\) filter can be regarded as a reactive filter in which contaminant removal occurs by self-filtration by virtue of in situ generated iron oxides. Thus, in batch and column systems, contaminant removal is not a property of reducing Fe\(^{0}\) but that of its corrosion products (adsorption and flocculation agents). Moreover, the well-documented contaminant reduction is not the cathodic reaction coupled to the anodic iron oxidative dissolution (aqueous iron corrosion) (see Section 6). In other words, the specificity of contaminants to the Fe\(^{0}/\)H\(_2\)O system is directly related to their adsorptive affinity onto iron oxides, hydroxides and oxyhydroxides. This evidence can be verified from published results on multiple contaminant systems and was explicitly demonstrated by Scott, Popescu, Crane, and Noubactep (2011) and Bilardi, Calabrò, Caré, Moraci,
transformations are subject to reaction kinetics. species and environmental conditions. However, possible

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effects in water (Tamura, 2008). The prevailing reaction,

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5 The nature of iron corrosion products

In the “Fe⁰ literature”, there is currently no agreement on

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Assi, Baydoun, Tuqan, & Bejjani, 2011), contaminant removal in any system depends on: (i) the amount of hydroxides/oxides/oxyhydroxides produced and (ii) the affinity of the contaminant of concern to these species. Accordingly, testing the suitability of Fe⁰ for the removal of any species in a single contaminant system is highly qualitative research.

6 Significance of iron corrosion products

Upon immersion any reactive Fe⁰ specimen is first covered

by a non-conducting, porous corrosion scale composed of iron (oxy)hydroxides. At this initial stage, dissolved species, including oxygen, can diffuse from the solution to the oxidative dissolution of Fe⁰, Eq. (1), and the reductive dissolution of Fe³⁺ oxides, Eq. (2), occur. The overall process has been termed autoreduction, and magnetite, Eq. (3), has been identified as the major reaction product (Odziemkowski & Simpraga, 2004).

\[
\begin{align*}
\text{Fe}^{0} + 2 \text{H}^+ & \rightarrow \text{Fe}^{2+} + \text{H}_2 \quad (1) \\
\text{Fe}^{0} + \text{Fe}_2 \text{O}_3 + 6 \text{H}^+ & \rightarrow 3 \text{Fe}^{3+} + 3 \text{H}_2 \text{O} \quad (2) \\
3 \text{Fe}^{3+} + 4 \text{H}_2 \text{O} & \rightarrow \text{Fe}_3 \text{O}_4 + 6 \text{H}^+ + \text{H}_2 \quad (3)
\end{align*}
\]

It is essential to note that Fe₃O₄ results from Fe⁰ generated in Eqs. (1) and (2). Although the documentation of autoreduction in short-term experiments is an excellent observation, it should be recalled that this observation was made in the context of rationalizing contaminant reductive transformation in Fe⁰/H₂O systems despite the initial presence of Fe³⁺ oxides (Scherer, Richter, Valentine, & Alvarez, 2000).

Regardless of the prevailing environmental conditions, an immersed reactive Fe⁰ specimen will be inevitably coated by an iron oxide layer. From the Fe⁰ surface to the aqueous solution, the evolution of the corrosion products follows the increasing order of the oxidation state (0, II, II/III and III). Two extreme sequences could be: (i) Fe⁰, FeO, Fe₂O₄, Fe₃O₄/FeOOH and (ii) Fe⁰, FeO, green rust, Fe₂O₄/FeOOH. Green rusts (e.g., [Fe²⁺₃Fe³⁺(OH)₈]²⁺[Cl·H₂O]) are unstable compounds containing divalent (Fe²⁺) and trivalent (Fe³⁺) iron (Bartzas, Komnitas, & Paspalaris, 2006; Chaves, 2005; Komnitas, Bartzas, & Paspalaris, 2006). The observation of each individual species depends on its stability under operational conditions. It is certain that FeO is not stable at low temperatures (Pourbaix diagrams). It is therefore not surprising that this phase has not been routinely reported (Odziemkowski & Simpraga, 2004). More stable green rust and magnetite (Fe₃O₄) have commonly been identified, but these are intermediates that could be further transformed. Fe₂O₄ could be regarded as the “natural” product of aqueous iron corrosion under anoxic conditions. In other words, identifying Fe₂O₄ is not knowledge acquisition. Rationalizing any deviation from the expected Fe₂O₄ would have been an interesting task.
the vicinity of the \( \text{Fe}^0/\text{hydroxides} \) interface. The cathodic reduction occurs at this interface. Later on, a less porous (but more conductive) magnetite scale is formed at the \( \text{Fe}^0 \) surface. From this stage on, the \( \text{Fe}^0/\text{Fe}_3\text{O}_4 \) interface is difficult to access for all corresponding species. However, electrons from the metal could still reach the \( \text{Fe}_3\text{O}_4/\text{hydroxides} \) interface. From this moment on, there is a delocalization of the cathodic area (see Section 7). Cathodic reactions can occur in the scale itself, but not at the \( \text{Fe}^0/\text{Fe}_3\text{O}_4 \) interface. Because iron oxides cannot permanently adhere to the \( \text{Fe}^0 \) surface (Dickerson et al., 1979), after some time of immersion, a decohesion of the whole oxide scale occurs and dissolved species can again reach the metal/oxides interface through microscopic cracks (Tamura, 2008). This has been traceably identified as the rationale for the suitability of iron corrosion, relevant for using \( \text{Fe}^0 \) for environmental remediation (Noubactep, 2010a,b).

In other words, knowledge acquisition here should have consisted of identifying the parameters influencing the cycles of formation/destabilization of oxide scales on \( \text{Fe}^0 \). The tangible fact that all intermediate corrosion products (including \( \text{Fe}^2\ ), \( \text{Fe}_3\text{O}_4 \), green rust, \( \text{H}_2/\text{H}^0 \)) could be present and contribute to contaminant reductive transformation within the hydroxide layer (chemical reaction) is obvious. Moreover, given the density of reducing agents in systems involving green rust, for example, it is difficult to credit \( \text{Fe}^0 \) with reducing capacities (electrochemical reaction) in \( \text{Fe}^0/\text{H}_2\text{O} \) systems (Jiao et al., 2009), even though it is traceably the parent of all available reducing species. Clearly, although iron corrosion is an electrochemical process, contaminant reduction in an \( \text{Fe}^0/\text{H}_2\text{O} \) system is mostly a chemical reaction. This knowledge was ahead of the occurrence of \( \text{Fe}^0 \) technology (Stratmann & Müller, 1994 and references cited therein).

### 7 Altering the course of mainstream science

As early as 1926, Walter G. Whitman, a chemical engineer from the Massachusetts Institute of Technology, introduced a review article on iron corrosion: “The selection of material for a review on corrosion is complicated by the breadth of the field, the variety of phenomena encountered and the conflict, of published opinion and theory. It therefore seems best to confine the discussion to certain features which have wide application and which have excited recent experimental research rather than to attempt anything in the nature of a complete bibliography of the subject”. Following this selection criteria, major aspects of aqueous iron corrosion, relevant for using \( \text{Fe}^0 \) for environmental remediation, should have been presented. In particular, segregation between a chemical and electrochemical reaction should have been the focus of more attention.

According to the electrochemical concept, iron oxidative dissolution takes place through a cell between two distinct areas of the \( \text{Fe}^0 \) surface. At the anodic area, the metal goes into solution (dissolution), whereas at least one corresponding reaction goes on simultaneously at the cathodic area. The current passes from the anode to the cathode through the solution and back to the anode through the \( \text{Fe}^0 \) body. The universal validity of the electrochemical nature of aqueous iron corrosion under environmental conditions is well established (Whitman, 1926). However, the chemical transformation of aqueous species in the presence of \( \text{Fe}^0 \) is not necessarily directly coupled to \( \text{Fe}^0 \) dissolution (electrons from the metal body). In fact, the surface of \( \text{Fe}^0 \) is always covered with a multilayered porous oxide scale which is rarely electronic conductive. Simultaneously, the oxide scale exhibits a certain adsorptive affinity to aqueous species and contains reducing agents (e.g., \( \text{Fe}^3\ ), green rust, \( \text{H}_2/\text{H}_2\)). All these reducing agents react with a chemical and not an electrochemical mechanism.

The disadvantage of \( \text{Fe}^0 \) technology has been that from its very early stage, electrochemical iron corrosion was coupled to contaminant reductive transformation. Data have been massively produced to support this view. Any argument challenging this view was severely combated or simply ignored (Noubactep, 2010b, 2011a,b). However, the conversion of available data into knowledge is an impossible task because the theory of the system is/was not given or established. In the absence of any theory of the system, there is no guide to test the validity of any hypothesis (Brenner, 2010).

From the disputed or non-adequately considered arguments, only five will be listed for illustration: (i) Lipczynska-Kochany, Harms, Milburn, Sprah, and Nadarajah (1994) questioned the sustainability of contaminant reduction by \( \text{Fe}^0 \) under environmental conditions; (ii) Schreier and Reinhard (1994) reported on a time lag between \( \text{Fe}^0 \) immersion (iron corrosion) and contaminant reductive transformation, this observation suggests that both reactions are not simultaneous; (iii) Farrell et al. (2001) clearly demonstrated that \( \text{Fe}^0 \) is mostly oxidized by water (the solvent); (iv) Lavine et al. (2001) could not identify the contribution of direct reduction (electrons from \( \text{Fe}^0 \)) in the process of nitrobenzene reduction in \( \text{Fe}^0/\text{H}_2\text{O} \) systems; and (v) Jiao et al. (2009) demonstrated that chemical reduction of carbon tetrachloride in \( \text{Fe}^0/\text{H}_2\text{O} \) systems is mediated by adsorbed hydrogen atoms produced during iron corrosion. These five points suggest that the discussion of the stoichiometry of reductive
transformation should not only be based on equations involving Fe⁰ (Gheju & Balcu, 2011).

8 Non-convincing mass balance

Equations similar to Eq. (4) are routinely used to discuss the process of contaminant removal in Fe⁰/H₂O systems.

\[ \text{Fe}^{0} + \text{Ox} \Rightarrow \text{Fe}^{2+} + \text{Red} \quad (4) \]

where Ox is the oxidized form of a contaminant which is transformed to the (hopefully) less soluble or less/ non-toxic reduced form (Red). The extensive majority of available studies have focused the mass balance discussion on Ox, Red and their intermediates. However, the iron balance has to be considered as well (Furukawa, Kim, Watkins, & Wilkin, 2002; Gould, 1982; Liu et al., 2013). In particular, the mass balance of Ox/Red should consider the fraction of these species that is enmeshed in the mass of iron corrosion products (Noubactep, 2009). To the best of the author’s knowledge, such an effort for complete mass balance has been only recently performed (Kishimoto, Iwano, & Narazaki, 2011). Accordingly, it is not surprising that “no carbon balances between reactants and products have ever been successfully done for many chlorinated hydrocarbons” (Lee, Rho, & Jahng, 2004).

For the proper design of an Fe⁰ filtration system, the reaction involving secondary reducing agents (e.g., Fe³⁺, H₂) must be considered, Eq. (5).

\[ \text{Fe}^{0} + \text{Ox} \Rightarrow \text{Fe}^{3+} + \text{Red} \quad (5) \]

This assertion is supported by the results of Gould (1982) who reported that 1.33 mol of Fe⁰ dissolved for each mol of Cr(VI) reduced. Such a high electron efficiency (extent of electron utilization during the Fe⁰ process) suggested that hydrogen generated during iron corrosion acts as a reducing agent for Cr(VI). In other words, Fe⁰ should be regarded as the generator of reducing agents (e.g., Fe³⁺, H₂) and adsorbents (e.g., Fe₂O₄, FeOOH).

Under environmental conditions, high electron efficiency as reported by Gould (1982) is not expected. For such situations, Liu et al. (2013) suggest a rational selection of Fe⁰ materials to maximize efficiency in the long term. Here an efficiency factor of 1/5 can be arbitrarily considered meaning that from 5 mol of Fe⁰ dissolved, only 1 is used for contaminant reduction. This assumption is conservative because the solvent is an oxidizing agent for Fe⁰. The overall importance of this assumption relies on the contribution of expansive iron corrosion to the process of porosity and permeability loss in Fe⁰-based filtration systems.

9 Porosity and permeability loss

Metallic iron (Fe⁰) is currently a standard reactive material for PRBs. Alternative materials are mostly compared to Fe⁰ or developed to overcome its weaknesses (Henderson & Demond, 2013). One fundamental weakness of Fe⁰ filtration systems is the progressive reduction of the hydraulic conductivity (permeability loss) due to the precipitation of solids and the formation of gases. Henderson and Demond (2013) reported that “the reduction in permeability is attributed to the formation of precipitates, although, in some cases, such as at the Copenhagen Freight Yard, enough H₂(g) was produced each day to fill 5% of the pore space”. This statement reflects the current state-of-the-art knowledge on the relative importance of processes determining permeability loss. However, the whole discussion has ignored the volumetric expansive nature of iron corrosion (Caré et al., 2013; Pilling & Bedworth, 1923).

When a reactive Fe⁰ is immersed, oxide scales are formed at the Fe⁰/H₂O interface. Pilling and Bedworth (1923) have established that the volume of any corrosion product is higher than that of the original metal. The ratio (η) between the volume of the expansive corrosion product and the volume of the parent iron is called the “expansion coefficient”. According to Caré, Nguyen, L’Hostis, and Berthaud (2008), η values vary from 2.08 to 6.40 for aqueous iron corrosion. The lowest η value corresponds to Fe₅O₄ as the sole corrosion product (anoxic conditions) and the largest to Fe(OH)₃·3H₂O (oxic conditions). These η values alone suggest that Fe⁰ filtration systems are more sustainable under anoxic conditions. Accordingly, in aboveground water treatment plants, Fe⁰ filters should be placed after oxygen consuming processes (e.g., slow sand filters) (Noubactep et al., 2012b).

The appropriate consideration of the volumetric expansive nature of iron corrosion implies that corrosion stops when there is no space for volumetric expansion. At this time, the system is clogged, no H₂ production or further reductive transformation are possible. A powerful tool to delay clogging is to reduce the proportion of Fe⁰, the generator of fouling precipitates. In other words, a properly designed Fe⁰ filtration system defines the optimal reactive permeability (more sand, less Fe⁰) and efficiency (more Fe⁰, less sand) for contaminant removal in the long term (Bilardi et al., 2013a,b; Noubactep, 2013b). Theoretical research has shown that the Fe⁰ volumetric proportion should not exceed 60% (Caré et al., 2013; Noubactep & Caré, 2010a,b, 2011; Noubactep et al., 2012b). First laboratory results indicated that the optimal volumetric Fe⁰ ratio in an Fe⁰:sand
mixture could be around 30% (Bilardi et al., 2013a,b; Miyajima, 2012; Miyajima & Noubactep, 2013).

An important aspect of volumetric expansion in connection with the low solubility of Fe under environmental conditions is that Fe species are left behind. Accordingly, an Fe mass balance is always needed to evaluate porosity loss due to iron corrosion (Fe oxides and hydroxides). Only after inherent corrosion products have been properly considered can the discussion of other factors be optimized. These factors include (i) H₂ evolution, (ii) precipitation of foreign species (e.g., CaCO₃), and (iii) precipitation of mixed species with iron (e.g., FeCO₃). Moreover, the characterization of Fe⁰ intrinsic reactivity is needed to evaluate the rates of iron corrosion under field conditions and discuss the evolution of permeability with time.

Another important aspect of volumetric expansion is that the initial filter is comparable to a conventional media filtration system (e.g., sand filter or pumice filter), but filtration efficiency is gradually improved as porosity is reduced by in situ generated iron corrosion products. In other words, a well-designed Fe⁰ filter is a self-filtration system whose performance increases with time at the expense of permeability loss (Dikinya, Hinz, & Aylmore, 2008). The presentation above has not addressed chemical transformations (e.g., oxidation, reduction) of contaminants. In other words, whether contaminants are reduced or not, they are removed by adsorptive size exclusion. This suggests that Fe⁰ particles could be regarded as “filter aids” in a sand filter (Yao, Habibian, & O’Melia, 1971). This conclusion is supported by relative low volumetric abundance of Fe⁰ in sustainable filters (actually ≤30%).

10 Summary

The past two decades have witnessed rapid progress in using metallic iron (Fe⁰) for environmental remediation. From the initial use of granular Fe⁰ as filling material for reactive barriers, systems for source zone remediation with injected nanoscale Fe⁰ have been developed as well. Research has produced a large volume of data which were intended to improve system design in general and non-site specific design in particular. Unfortunately, the whole effort was data oriented and the results achieved should be regarded as very modest.

The present article has shown that a proper understanding of the chemical and physical processes occurring in Fe⁰/H₂O systems is possible from the knowledge on iron corrosion and water filtration preceding the occurrence of “iron technology”. Moreover, this knowledge has been constantly recalled within the Fe⁰ research community, but has never gained legitimate attention. However, research on “iron technology” was fruitful as it could induce the acceptance and even the establishment of this innovative technology. Accordingly, coming back to the highways of mainstream iron corrosion science would accelerate further development of this technology and could mediate its universal acceptance.

The major challenge for Fe⁰ technology is to understand it as a filtration system. Once this is done, it will be relatively easy for active research groups to re-evaluate available data and complete them with target well-designed experiments to acquire necessary knowledge. A good starting point could be the characterization of the intrinsic reactivity of available commercial Fe⁰ and its classification into classes and design rules of thumb such as: “for a groundwater from type A”, use a Fe⁰:sand ratio of x:y for “Rheinfelden Fe⁰” or z:t for “Peerless Fe⁰”. The relative geometry (shape and size) of both materials should be characterized. Once a database of such systems is available, prospective work could continue by testing other materials such as anthracite, MnO₂, pumice or zeolites. It could be expected that systematic research based on these guidelines could enable a thorough understanding of the Fe⁰/H₂O system within 10 years.

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References


Bilardi S, Calabrò PS, Carè S, Moraci N, Noubactep C. Effect of pumice and sand on the sustainability of granular iron beds for the removal of Cu²⁺, Ni²⁺, and Zn²⁺. Clean Soil Air Water 2013a; 365: 207 – 212.


Miyajima K. Optimizing the design of metallic iron filters for water treatment. Freiberg Online Geosci 2012; 32: 60 (http://tu-freiberg.de/geo/fog).


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Graphical abstract

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**Metallic iron for environmental remediation: the long walk to evidence**

**Review:** The exploitation of the huge potential of using metallic iron for water treatment is delayed by a non-scientific approach.

**Keywords:** corrosion science; environmental remediation; water treatment; zero-valent iron.