Modelling the permeability loss of metallic iron water filtration systems

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Abstract

Over the past 30 years the literature has burgeoned with in-situ approaches for groundwater remediation. Of the methods currently available, the use of metallic iron (Fe0) in permeable reactive barrier (PRB) systems is one of the most commonly applied. Despite such interest, an increasing amount of experimental and field observations have reported inconsistent Fe0 barrier operation compared to contemporary theory. In the current work, a critical review of the physical chemistry of aqueous Fe0 corrosion in porous media is presented. Subsequent implications for the design of Fe0 filtration systems are modelled. The results suggest that: (i) for the pH range of natural waters (> 4.5), the high volumetric expansion of Fe0 during oxidation and precipitation dictates that Fe0 should be mixed with a non-expansive material; (ii) naturally-occurring solute precipitates have a negligible impact on permeability loss compared to Fe0 expansive corrosion; and (iii) the proliferation of H2 metabolising bacteria...
may contribute to alleviate permeability loss. As a consequence, it is suggested that more
emphasis must be placed on future work with regard to considering the Fe\textsuperscript{0} PRB system as a
physical (size-exclusion) water filter device.

**Keywords:** Deep-bed filtration, Hydraulic conductivity, Modelling, Permeability loss,
Zerovalement iron.

**Acronym List**

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<th>Acronym</th>
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<tr>
<td>ITRC</td>
<td>Interstate Technology &amp; Regulatory Council</td>
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<td>PRB</td>
<td>Permeable reactive barrier</td>
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<td>RZ</td>
<td>Reactive Zone</td>
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<td>ZVI</td>
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1 Introduction

Permeable reactive barriers containing metallic iron as a reactive filler material (Fe\textsuperscript{0} PRBs) is
an established technology for groundwater remediation [1-10]. At present, more than 120 Fe\textsuperscript{0}
PRBs have been installed worldwide, and effective performance has typically been reported
[10-13]. Fe\textsuperscript{0} PRBs typically contain either pure Fe\textsuperscript{0} or a mixture of Fe\textsuperscript{0} and another material,
such as gravel or sand. The incorporation of a secondary material is typically employed either
to meet design requirements, cost, or to limit permeability loss. In such cases, potential
drawbacks on the kinetics of contaminant removal must be considered [14]. However, some
available experimental results from batch [15,16] and column [14,17] studies suggest that
admixing pumice/sand to Fe\textsuperscript{0} is beneficial for the process of contaminant removal. Therefore,
the recent statement of Ulsamer [13] that “there is no conclusive evidence that a sand/iron mix
is better or worse than a pure iron barrier” can be considered the current state-of-the-art.

In addition, the challenge of determining the fundamental mechanisms which govern
hydraulic conductivity (permeability) loss is yet to be properly addressed [10,11,13,18,19]. At
present it is suggested that the mechanism of permeability loss in Fe\textsuperscript{0} PRBs is due to the
accumulation of insoluble minerals within the PRB pore network [10,13]. Relevant minerals include siderite (FeCO$_3$), aragonite (CaCO$_3$), and iron (hydr)oxides (e.g. Fe(OH)$_2$, Fe(OH)$_3$, FeOOH, Fe$_2$O$_3$, Fe$_3$O$_4$) [10,13,20-26]. Another mechanism reported attributes the permeability loss to the build-up of H$_2$ gas, formed due to the hydrolysis of water during Fe$^0$ corrosion [11,27,28]. However, as H$_2$ is a key source of energy for numerous different microorganism species [23,29-31], the contribution of H$_2$ to the process of Fe$^0$ PRB permeability loss has been ascribed as minor [32].

The theory that Fe$^0$ PRB permeability loss is predominantly due to the accumulation of insoluble minerals within pore volumes was recently challenged by Henderson and Demond [11]. The authors cited that whilst natural groundwater constituents (e.g. carbonates) and contaminant species can occur in subsurface concentrations of several hundred parts per million (or mg per litre), the mass/volume occupied by the mineral precipitates will be minor compared to the large amount required to significantly impair the permeability of an average permeable reactive barrier system. Based on this premise they attributed the permeability loss to the accumulation of H$_2$ gas, and suggested periodical venting to prevent build-up. All studies to date, however, have overlooked the role of the volumetric expansive iron corrosion products [33-36] in PRB permeability loss.

In the current work, a multidisciplinary theoretical approach has been applied to analyse the relationship between the extent of Fe$^0$ depletion and permeability loss in Fe$^0$ beds (including water filters and PRBs), by linking: contemporary knowledge of the mechanisms which govern contaminant removal by Fe$^0$ [37]; with mathematical modelling mass conservation equations. Much of the impetus for this work originates from recent work summarized in Noubactep et al. [38] wherein the advantages of admixing non-expansive materials to Fe$^0$ within Fe$^0$ filtration systems are discussed. For the sake of clarity, the basic conservation equation for the oxidative dissolution of iron will be given.

2 Conservation equation of iron corrosion at pH > 4.5
2.1 Basic conservation equation

The basic constitutive equation expressing the overall conservation of mass of any chemical element \((j)\) consumed in a chemical reaction relates volume \((V)\), dry bulk density \((\rho)\), and chemical composition \((C)\) and mass fluxes \((m)\) into or out of a system [39]:

\[
V_p\rho_p C_{j,p}/100 + m_{j,\text{flux}} = V_w\rho_w C_{j,w}/100
\]  

(1)

The first term of Eq. 1 expresses the mass of element \(j\), contained in the original material before reaction, subscripted as \(p\). It is given by the product of volume \((V\ \text{in cm}^3)\), dry bulk density \((\rho \ \text{in g/cm}^3)\), and elemental concentration \((C \ \text{in weight \%})\). The mass of element \(j\) introduced into or out of the considered volume is indicated as \(m_{j,\text{flux}}\) and is added to the mass of \(j\) in the system. Fluxes \((m_{j,\text{flux}})\) are positive if they enter the system and negative if they exit the system. On the right-hand side of Eq. 1, the mass of element \(j\) contained in the volume of reaction products, subscripted \(w\), is given by the product of the new volume, dry bulk density, and element concentration.

2.2 Conservation equation of iron corrosion at pH > 4.5

For iron corrosion, the element of concern is iron \((j = \text{Fe})\) which is distributed between the original metallic iron \((\text{Fe}_0 = \text{ZVI})\) and various iron hydroxides and oxides \((w = \text{ox})\). Eq. 1 can therefore be written as:

\[
V_{\text{ZVI}}\rho_{\text{ZVI}} C_{\text{Fe,ZVI}} + m_{\text{Fe,flux}} = V_{\text{ox}}\rho_{\text{ox}} C_{\text{Fe,ox}}
\]  

(2)

For pH > 4.5 the solubility of iron is very low and the flux of Fe \((m_{\text{Fe,flux}})\) can be largely neglected assuming that water flow rate is slow enough that the dissolution/precipitation reactions are at pseudo-equilibrium. Eq. 2 can be re-written as:

\[
V_{\text{ZVI}}\rho_{\text{ZVI}} C_{\text{Fe,ZVI}} = V_{\text{ox}}\rho_{\text{ox}} C_{\text{Fe,ox}}
\]  

(2a)

Eq. 2a suggests that \(V_{\text{ox}}\) (iron oxide) must be larger than \(V_{\text{Fe}}\) (metallic iron) because all iron (hydr)oxides are less dense than Fe\(^0\) (Tab. 1).

2.3 Volumetric strain
With regard to iron corrosion driven volume changes, there are three possibilities: (i) volumetric compression \((V_{ZVI} > V_{ox})\), (ii) isovolumetric transformation \((V_{ZVI} = V_{ox})\), and (iii) volumetric expansion \((V_{ZVI} < V_{ox})\). Accordingly, volumetric changes should be determined experimentally. This is accomplished by using the classical definition of strain, \(\varepsilon\), the ratio of volume change in a process to the initial volume (Eq. 3):

\[
\varepsilon = \frac{(V_{ox} - V_{ZVI})}{V_{ZVI}} = \frac{V_{ox}}{V_{ZVI}} - 1 \tag{3}
\]

Eq. 3 suggests that the volumetric strain is positive because \(\frac{V_{ox}}{V_{ZVI}} \geq 2.1 [35]\).

In the next section, a new approach for the discussion of permeability loss will be given. This exercise will be based on the recent paper by Henderson and Demond [11].

### 3 Permeability loss in Fe\(^{0}\)/H\(_2\)O systems

The purpose of this section is to discuss the relative importance of mineral precipitation, gas production and expansive iron corrosion for permeability loss in Fe\(^{0}\)/H\(_2\)O systems. Expansive iron corrosion products included rust. To this end, the species discussed by Henderson and Demond [11] will be considered individually (Table 1).

A cylindrical column apparatus for Fe\(^{0}\) filtration has an internal diameter \((D)\), a reactive length \((H_{rz})\), and a subsequent total volume \(V_{rz}\) \((V_{rz} = \pi D^2 H_{rz}/4)\). \(H_{rz}\) may be a fraction of the length of the column apparatus \((H_{rz} \leq H)\). A column may also contain several reactive zones. The discussion herein is limited to a single reactive zone. The ratio of the initial volume of the void space (inter-particular porosity) is \(\Phi_0\) and the volume of pore is \(V_p = \Phi_0 V_{rz}\). The volume occupied by the solid particles \(V_{solid}\) is \(V_{solid} = (1 - \Phi_0) V_{rz}\). Solid particles include Fe\(^{0}\) and additives (e.g. gravel, pumice, sand), assumingly having the same size and shape (roundness or sphericity). The following cylindrical column apparatus used by Henderson and Demond [11] is considered: \(D = 5\) cm, \(H_{rz} = H = 25\) cm, a subsequent \(V_{rz} = 491.1\) cm\(^3\), and initial porosities \((\Phi_0)\) of 0.62. \(\Phi_0 = 0.62\) is also from ref. [11].
The challenge of the current work is to evaluate which quantity of each fouling species (iron corrosion products) is necessary to occupy the initial pore volume (Vp).

3.1 Filling the pore volume with individual minerals and H₂ gas

In this section, Eq. (4) assumes that Fe⁰ is oxidized by water. The initial pore volume (Vp) is filled entirely by corrosion products (H₂ and FeII/FeIII species):

\[
x \text{Fe}^0 + y \text{H}_2\text{O} \Rightarrow \text{Fe}_x\text{O}_y + y \text{H}_2 \uparrow \tag{4}
\]

\[
t = 0 \quad n_0 \quad 0 \quad 0
\]

\[
t > t_0 \quad n_0*(1 – \alpha) \quad n_0*\alpha/x \quad y*n_0*\alpha/x
\]

\[
t > t_0 \quad x*n’_0*(1 – \alpha) \quad \alpha*n’_0 \quad y*n’_0*\alpha
\]

It is considered that the number of moles \(n_0\) of Fe⁰ at time \(t = 0\) \((t_0)\) is a multiple of \(n’_0\) \(n_0 = x*n’_0\). Accordingly, at \(t_0\), the reactive zone contains only \(x*n’_0\) Fe⁰ (no oxide and no hydrogen). At each time \(t\) \((t > t_0)\), the residual number of moles of Fe⁰ is \(x*n’_0*(1 – \alpha)\), the number of mole of generated oxide is \(\alpha*n_0/x = \alpha*n’_0\) and the number of mole of H₂ is \(y*n_0*\alpha/x = y*n’_0*\alpha\) where \(\alpha\) is the fraction of the initial amount of Fe⁰ which is depleted as a function of time \(t\). For iron hydroxides \((\text{Fe(OH)}_n)\) and carbonate \((\text{FeCO}_3)\), the stoichiometry of oxygen is taken as the value of “\(x\)” \((y = x)\) because each mole of Fe releases one mole of H₂ \(\text{for n = 2}\).

Knowing the molar volume of individual oxides and H₂ (Tab. 1), the degree of occupation of the initial pore volume (Vp) can be evaluated. The reactive zone is clogged when enough corrosion products \((\text{Fe}_x\text{O}_y \text{ and H}_2)\) are produced to completely fill Vp. In other words, bed clogging corresponds to Eq. (5):

\[
V_{ZVI} + V_{ox} + V_{H2} = V_{rz} \tag{5}
\]

The volume \(V_i\) occupied by a species \(i\), is the product of its molar volume by the number of moles. The equation of the clogging can be written as (Eq. 5a):

\[
V_{m,ZVI}*x*n’_0*(1 – \alpha) + V_{m,ox}*n’_0*\alpha + V_{m,H2}*n’_0*y*\alpha = V_{rz} \tag{5a}
\]
To have $\alpha$ values for individual oxides, it is sufficient to solve Eq. 5a. The solution is given by Eq. 5b:

$$\alpha = \left[ V_{rz}/x*n'_{0} - V_{m,ZVI} \right] / \left[ V_{m,ox}/x + y/x*V_{m,H2} - V_{m,ZVI} \right]$$

The porosity of granular sandy beds used in sand filters ranges from 0.40 to 0.50 (average of 0.45) [41]. The porosity of the filtration bed depends on several factors including grain size, grain size distribution and shape (sphericity) of used particles [42]. The sphericity of the medium is a measure of its roundness and ranges from 0.70 (angular grains) to about 0.90 (grains rounded by water or wind) [41,43].

The volume of Fe$^0$ ($V_{Fe}$) in the pure Fe$^0$ system (100 % Fe$^0$) depends on the compactness C or the porosity $\Phi$ ($V_{Fe} = C*V_{RZ} = (1-\Phi)*V_{RZ}$). Reported operational values for the porosity of Fe$^0$ systems vary between 40 and 70 % [10,11,15]. Calculations are made for the extreme values of the porosity reported in peer-reviewed journal articles (36 and 62 %). $\Phi_0 = 36 \%$ corresponds to the ideal case of spherical materials [38]. The initial number of moles of Fe$^0$ ($n_0$) corresponding to the extreme cases are 41.4 ($\Phi_0 = 36 \%$) and 24.6 ($\Phi_0 = 62 \%$).

Calculations (Tab. 2) showed that if H$_2$ does not escape from the reactive zone, the consumption of less than 0.1 % of the initial amount of Fe$^0$ will be sufficient to clog the systems. If this was likely to occur, the Fe$^0$ filtration technology would have not been possible.

Calculations assuming total escape of H$_2$ gas out of the reactive zone ($V_{m,H2} = 0$ in Eq. 5b) indicate that 16 to 62 % of Fe$^0$ can be depleted just at system clogging ($\Phi_{te} = 0 \%$) when the initial porosity is 36 %. For $\Phi_0 = 62 \%$, 46 to 100 % Fe$^0$ could be depleted just at system clogging ($\alpha \geq 0.46$). In other words, the sustainability of a Fe$^0$ filtration system depends strongly from its initial porosity ($\Phi_0$).

The results herein suggest that, for $\Phi_0 = 36 \%$, when the main corrosion product is Fe$_3$O$_4$, only 58 % of Fe$^0$ is consumed just at system clogging. This value in agreement with the value
of 51% reported in former works [38]. The difference corresponds to different values used for the volumetric expansion coefficient (\(\eta\)); \(\eta = 1.97\) herein vs. \(\eta = 2.08\) in ref. [37]. However, this approach fails to consider the in-situ generation of colloidal Fe\textsuperscript{II}/Fe\textsuperscript{III} species and their further transformation to hydroxides and oxides [44,45].

Eq. 5b describes a pure iron bed (100% Fe\textsuperscript{0}). In the case that Fe\textsuperscript{0} is admixed with a non expansive additive (e.g. gravel, pumice, sand) the initial number of moles of iron (\(n_0\)) has to be corrected to the fraction of \(n_0\) corresponding to the volumetric proportion of Fe in the reactive zone, e.g. \(n_0/2\) for a system containing 50% Fe\textsuperscript{0} (v/v) and the balance amount of a non porous material.

The results from Tab. 2 suggest that, at \(\Phi_0 = 36\%\), pure Fe\textsuperscript{0} beds are not sustainable as a rule (see section 3.2.2). For larger initial porosity (\(\Phi_0\)), more sustainable systems are obtained. This result was already theoretically achieved by admixing Fe\textsuperscript{0} and porous media (e.g. pumice). However, increased initial porosity as discussed here results from the geometry (size, shape) of used media (e.g. Fe\textsuperscript{0}, sand, gravel).

The influence of the shape of the Fe\textsuperscript{0} particles on the Fe\textsuperscript{0} bed porosity is schematically represented in Fig. 1 as spherical (left) and cylindrical (right) Fe\textsuperscript{0} particles (black) are progressively transformed to oxides (grey - rust). Fig. 1 confirms the fact that packed beds of spherical media are the most compact [46-49]. This delineates the importance of characterizing Fe\textsuperscript{0} and sand materials for their uniformity and sphericity and the resulting bed for its compactness (porosity).

Another important feature seen in Tab. 2 (\(\alpha\) and \(\alpha'\) values) is that regardless from the abundance of Fe\textsuperscript{0} in the system, bed clogging due to H\textsubscript{2} gas production is likely to occur prior to the consumption of 0.1% Fe\textsuperscript{0}. However, under the experimental conditions considered by Henderson and Demond [11], gas accumulation is unlikely since the solutions were pumped in upflow at a flow rate of 0.7 mL/min into the columns. In addition, under field conditions,
H₂ consuming bacteria are ubiquitous [29]. In such cases, clogging is therefore more likely to result from enhanced (bio-)stimulation (biofilm growth) and not from H₂ accumulation.

The estimations in this section clearly show that if H₂ was primarily responsible for bed clogging, then it is unlikely that the Fe⁰ PRB technology would have been effective on medium to long-term timescales as observed in the field. PRB clogging would have been prevalent before a fraction (less than 0.1 %) of the Fe⁰ had corroded. However, H₂ gas may contribute to permeability loss in association with particle ‘cementation’ (compaction) by nascent iron hydroxides. In this case, compaction prohibits H₂ escape and increases flow resistance for pumped solutions.

### 3.2 The process of permeability loss in Fe⁰/H₂O systems

In this section, a contemporary evaluation of permeability loss in the Fe⁰/H₂O system is given. The methodology is explicitly presented in ref. [38]. In the current work the following assumptions apply:

(i) Uniform Fe⁰ corrosion: the radius reduction of spherical or cylindrical Fe⁰ particles is the same for all particles;

(ii) the volume of the reactive zone (V_rz) remains constant and the volume of granular materials (e.g. sand) is not modified by the corrosion process;

(iii) Fe⁰ corrosion products are fluid enough to progressively fill available pore space.

As shown in section 2.3, iron corrosion occurs with concurrent volumetric expansion (\(\eta = V_{\text{ox}}/V_{\text{ZVI}} > 1\)). The excess volume of Fe⁰ imbued by corrosion product formation is given by V_{\text{excess}} in Eq. 6. By definition, V_{\text{excess}} is the difference between \(V_{\text{ox}}\) and \(V_{\text{ZVI}}\) (Eq. 6).

\[
V_{\text{excess}} = (\eta - 1) \ast V_{\text{ZVI}} \tag{6}
\]

The Fe⁰ filtration system is clogged when the volume \(V_{\text{excess}}\) is equal to the initial intergranular voids (\(V_p\)). “\(V_{\text{ZVI}}\)” in Eq. 6 represents the volume of Fe⁰ in a pure Fe⁰ bed. However, as discussed in sections 1 and 3.1, Fe⁰ should be only a fraction of \(V_{\text{solid}}\) (\(V_{\text{ZVI}} = \tau_{\text{ZVI}} \ast V_{\text{solid}}\), with \(\tau_{\text{ZVI}} \leq 1\)). Eq. 6 can be rewritten as:
Eq. 6a suggests that, for every \( \eta \) value (i.e. every oxide), \( V_{\text{excess}} \) is a linear function of \( \tau_{\text{ZVI}} \). To find out at what extent \( \tau_{\text{ZVI}} \) contributes to complete pore filling, it is sufficient to graphically solve Eq. 6a for \( V_{\text{excess}} = V_p \). Practically, there are two equivalent approaches: (i) solving \( V_{\text{excess}} - V_p = 0 \) or (ii) solving \( \frac{V_{\text{excess}}}{V_p} = 1 \). The second approach is adopted in this work.

The solution of Eq. 6a (clogging) is the interception of the line \( \frac{V_{\text{excess}}}{V_p} = f(\tau_{\text{ZVI}}) \) with the line 100 % (Fig. 2). Before discussing the actual evolution of the porosity, some fundamental aspects for the solution of Eq. 6a will be given.

### 3.2.1 Fe\(^0\) filtration systems

To date, Fe\(^0\) particles have been widely reported as successful for water treatment [50-53]. However, a holistic understanding of the Fe\(^0\)/H\(_2\)O system is yet to be achieved.

Fig. 2 represents the principle of Fe\(^0\) filtration beds. The origin (point O) represents a Fe\(^0\)-free filter (e.g. activated alumina, activated carbon, gravel, pumice, sand, zeolite) and point I(100,100) represents an “ideal Fe\(^0\)-based filter” which becomes 100 % clogged concurrent with 100 % Fe\(^0\) depletion (\( \frac{V_{\text{excess}}}{V_p} = 1 \)). The line OI divides the graph into two halves. Below OI, \( \frac{V_{\text{excess}}}{V_p} < 100 \) and the system is not clogged at Fe\(^0\) depletion. Above OI, \( \frac{V_{\text{excess}}}{V_p} > 100 \) and the system is clogged before Fe\(^0\) depletion (a proportion of Fe\(^0\) is wasted). Thus, Fig. 2 can be regarded as a useful reference tool for future work within this field. Relevant parameters to complement Fig. 2 that will be investigated in future work include: (i) the intrinsic reactivity of Fe\(^0\); (ii) the shape and size of Fe\(^0\); (iii) the shape and size of sand; (iv) the dimensions and the geometry of the Fe\(^0\) bed; (v) the thickness of the Fe\(^0\)/sand layer; (vi) the proportion of Fe\(^0\) in the Fe\(^0\)/sand layer; and (vii) the water flow velocity.

Point O in Fig. 2 represents all filtration designs without Fe\(^0\) (or another metallic element). These include conventional slow sand filters (SSF), biosand filters (BSF) and iron oxide-coated sand filters. Considering filtration designs which entirely contain sandy materials, point O can be limited to BSF and SSF. SSF have been used for water treatment since 1840 in...
Dijon/France by Henry Darcy [54]. BSF have been used for water treatment at household level for over 20 years [55,56]. However, despite intensive research on BSF, their operating mode is yet to be completely understood [42,43,55]. For example, there are no established comprehensive design criteria for BSF [41,55,57]. Accordingly, the reproducibility and comparison of reported results from one setting to another is problematic. To fill this gap, Kubare and Haarhoff [41] have provided the most recent systematic review for a rational design of BSF. A Fe\(^0\) filtration system (Fig. 2) can be regarded as a modification of a SSF or BSF (point O). Therefore, it is essential to carefully develop rational and comprehensive engineering design criteria. In this effort, designing tools for BSF would be very helpful [41,55].

3.2.2 The role of initial porosity in Fe\(^0\) bed clogging

The theoretical discussion of Fe\(^0\) PRB porosity until now was focused on the case of maximum compactness for which the initial porosity is 0.36 (\(\Phi_0 = 36\) %) [32]. For such systems, a pure Fe\(^0\) bed is clogged when less than 60 % of the initial amount of Fe\(^0\) is depleted (section 3.1). According to Fig. 1, for \(\Phi_0 = 36\) %, all Fe\(^0\) beds are situated above line OI. However, significantly larger porosity values have typically been reported in the literature, the highest being 62 % by Henderson and Demond [11]. Accordingly, this section discusses the evolution of the porosity of a conventional sand filter (0 % Fe\(^0\)) as it is progressively transformed to a pure Fe\(^0\) filter (100 % Fe\(^0\)). Particular attention is paid to the extreme values of the porosity (\(\Phi_0 = 36\) and 62 %). The results are summarized in Fig. 3.

The ideal line OI is not represented in Fig. 3 for clarity. Instead the point I(100,100) is represented. Fig. 3a (\(\Phi_0 = 0.36\)) shows clearly that all systems are clogged before Fe\(^0\) depletion has been occurred. In contrast, Fig. 3b shows that, for an initial porosity (\(\Phi_0\)) of 0.62, Fe\(^0\) beds are sustainable if magnetite (Fe\(_3\)O\(_4\)), maghemite (\(\gamma\)-Fe\(_2\)O\(_3\)) and hematite (Fe\(_2\)O\(_3\)) are the sole iron corrosion products. Additionally, it shows that ferrous hydroxide (Fe(OH)\(_2\)) is the “ideal corrosion product” for the Fe\(^0\) PRB to clog concurrent with Fe\(^0\)
depletion. With the formation of ferrous hydroxide, magnetite, maghemite and hematite being more prevalent in anoxic conditions, it can therefore be stated that Fe$^{0}$ PRBs are most ideally suited for oxygen depleted or anoxic conditions.

Magnetite ($x_{\text{Fe}} = 72.4 \%$, Tab.1) may result from Fe(OH)$_2$ dehydration under anoxic conditions and is therefore the sole mineral, that is likely to be quantitatively generated from anoxic Fe$^{0}$ corrosion.

### 3.2.3 Discussion

The presentation until now has focused on the evolution of the permeability loss as a key factor for the sustainability of Fe$^{0}$ PRB systems. A Fe$^{0}$ filtration system is sustainable only if it can maintain hydraulic (permeability) performance while also remaining effective for pollutant removal. In other words, a permeable but non reactive Fe$^{0}$ filtration system is useless.

A Fe$^{0}$ filtration system can be considered both a chemical and physical water filter device, with its efficacy dictated by progressive expansion/compression cycles during aqueous corrosion [52]. In a Fe$^{0}$ filtration system, chemical reactions included (i) iron oxidative dissolution, (ii) polymerisation of iron hydroxides and, (iii) subsequent precipitation of hydroxides and oxides. Quantitative chemical transformations (oxidation/reduction) of dissolved species may also occur. However, resulted species must be removed from the aqueous phase by a physical process: adsorption, occlusion, size-exclusion. Accordingly, Fe$^{0}$ is not a strong reducing agent under environmental conditions as widely accepted [5-7,10].

More importantly, reduction is not a stand alone contaminant removal mechanism [58-61]. Rather, Fe$^{0}$ is a generator of contaminant scavengers for reactive filtration [44,62-65]. While adsorptive filtration has been mostly used for metal removal [62-65], the affinity of organic compounds for iron hydroxide/oxides (corrosion products) is well documented [66-71]. For example, Saha et al. [71] investigated the adsorptive removal of seven different dyes on iron
oxide nanoparticles an reported on enhanced adsorption capacity of the dyes containing hydroxyl (-OH) (erichrome black-T, bromophenol blue, bromocresol green, and fluorescein).

For the proper scaling of Fe\(^0\)-supported sand filters as reactive filtration device, factor sustaining size exclusion should be understood and optimised [72]: (i) the pore size must be small enough for sufficient contaminant removal; or (ii) used Fe\(^0\) must be reactive enough to produce a sufficient amount of ‘scavengers’ as a function of time. Alternatively, the thickness of the Fe\(^0\) PRB can be increased to improve the devices filtration capacity.

This highlights the importance of characterizing the intrinsic reactivity of Fe\(^0\) materials prior to application [73]. Ideally, the selection of a Fe\(^0\) material for a particular site should be governed by its intrinsic reactivity (and porosity when incorporated in the PRB system) and the expected impact of local geochemical (and geophysical) conditions on these factors. In cases where contaminant breakthrough was observed despite insignificant permeability loss, two explanations can be suggested: (i) the material is not reactive enough to generate “scavengers” in sufficient quantities, (ii) clogging of the entrance zone has disturbed the flow regime and preferential flow paths are created in the system. Preferential flow paths significantly impair the contact of flowing water with bed media (collectors, iron, sand).

4 Conclusions

Correlating the fundamental relationship between Fe\(^0\) PRB permeability loss and groundwater chemistry is extremely important for the design of sustainable Fe\(^0\) remediation systems. Further developments require knowledge of the intrinsic reactivity of Fe\(^0\), the rate of the formation of corrosion products and the role of foreign detrital minerals. Using mathematical modelling, the present communication challenges both the prevailing view and the contribution of Henderson and Demond [11]. An extensive mass balance analysis of aqueous iron corrosion has been used to show that volumetric expansion is the major control on permeability loss. It has been shown that, whilst Fe\(^0\) filtration systems (including PRBs) operating in anoxic (phreatic zone) conditions can exhibit limited permeability loss due to Fe\(^0\).
corrosion product formation, Fe$^0$ filtration systems operating in oxic (vadose zone) conditions exhibit significantly high permeability loss. It can therefore be concluded that admixing Fe$^0$ with a non expansive materials (e.g. gravel, MnO$_2$, pumice, sand) is a prerequisite for any sustainable Fe$^0$ filtration systems operating in the near surface geosphere.

The present work and related studies have delineated the early development of the Fe$^0$ PRB technology that was marked by empirical designs [37,38,74,75-80]. Field experiences from more than 120 reactive barriers and an innumerable numbers of filters (including laboratory columns) worldwide should be used to continuously refine this innovative technology.

Clearly the Fe$^0$ technology should now be translated into rational engineering design criteria. As there are no established comprehensive design criteria for Fe$^0$ beds, the reproducibility and comparison of available results is problematic. For example, despite the established significance of particle shape and size on the permeability, these parameters are not routinely given when describing operational conditions. Similarly, the initial porosity is not always given and the contribution of iron corrosion products to its filling was not properly addressed.

A tentative guideline for future laboratory experiments can also be concluded: (i) assess the intrinsic reactivity of used Fe$^0$, (ii) define the size and sphericity of all used materials (Fe$^0$ and admixing materials), (iii) consider the surface roughness of Fe$^0$ and sand grains, (iv) characterize the dimension and the composition of used columns, (v) evaluate the porosity of resulted columns, (vi) characterize used initial solutions (e.g. pH, Eh, O$_2$ level, contamination), (vii) record the time dependant volume of the column effluent, and (viii) characterize the column effluent for pH, Eh, dissolved iron, target contaminants.

Acknowledgments

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References


www.itrcweb.org (access: 09.03.2012)


[12] N. Muchitsch, T. Van Nooten, L. Bastiaens, P. Kjeldsen, Integrated evaluation of the performance of a more than seven year old permeable reactive barrier at a site


Table 1: Some characteristics of metallic iron (Fe$^0$) and its main corrosion products commonly identified in Fe$^0$ PRBs. “x” is the weight percent of Fe in the phase. As a rule, oxides formed under anoxic conditions exhibit larger x values. “$\eta$” is the calculated coefficient of volumetric expansion. Phase parameters are compiled from Balasubramanian et al. [40] and Henderson and Demond [11].

<table>
<thead>
<tr>
<th>Phase</th>
<th>Name</th>
<th>Structure</th>
<th>Density (g/cm$^3$)</th>
<th>$V_m$ (cm$^3$/mol)</th>
<th>x (%)</th>
<th>$\eta$ (-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$^0$</td>
<td>Iron metal</td>
<td>bcc</td>
<td>7.86</td>
<td>7.6</td>
<td>100.0</td>
<td>-</td>
</tr>
<tr>
<td>Fe(OH)$_3$</td>
<td>Fe$^{III}$ hydroxide</td>
<td>perovskite-like</td>
<td>3.1</td>
<td>34.4</td>
<td>52.0</td>
<td>4.53</td>
</tr>
<tr>
<td>FeCO$_3$</td>
<td>Siderite</td>
<td>Trigonal</td>
<td>3.83</td>
<td>29.3</td>
<td>48.3</td>
<td>3.86</td>
</tr>
<tr>
<td>Fe(OH)$_2$</td>
<td>Fe$^{II}$ hydroxide</td>
<td>Trigonal</td>
<td>3.4</td>
<td>26.4</td>
<td>62.2</td>
<td>3.47</td>
</tr>
<tr>
<td>$\alpha$-FeOOH</td>
<td>Goethite</td>
<td>Orthorhombic</td>
<td>4.28</td>
<td>20.3</td>
<td>62.9</td>
<td>2.67</td>
</tr>
<tr>
<td>$\gamma$-Fe$_2$O$_3$</td>
<td>Maghemite</td>
<td>Cubic</td>
<td>4.69</td>
<td>29.1</td>
<td>70.0</td>
<td>1.91</td>
</tr>
<tr>
<td>$\alpha$-Fe$_2$O$_3$</td>
<td>Hematite</td>
<td>Trigonal</td>
<td>5.3</td>
<td>30.1</td>
<td>70.0</td>
<td>1.98</td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td>Magnetite</td>
<td>Cubic</td>
<td>5.175</td>
<td>45.0</td>
<td>72.4</td>
<td>1.97</td>
</tr>
</tbody>
</table>
Table 2: Estimation of the extent of Fe\(^0\) depletion (\(\alpha\) value in \%) in the column of Henderson and Demond [11] for two values of the initial bed porosity. \(\alpha\) and \(\alpha_1\) correspond to \(\Phi_0 = 36\) \% when \(H_2\) remains in the system or escapes respectively and \(\alpha'\) and \(\alpha'_1\) correspond to \(\Phi_0 = 62\) \% when \(H_2\) remains in the system or escapes respectively. It is seen that in all cases the initial porosity is filled by gas when less than 0.1 \% of the initial mass of Fe\(^0\) is corroded. A value of 100 \% is related to a system which is not clogged when Fe\(^0\) is depleted.

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>(\alpha) values (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(\alpha)  (\alpha_1) (\alpha') (\alpha'_1)</td>
</tr>
<tr>
<td>Maghemite</td>
<td>Fe(_2)O(_3)</td>
<td>0.01</td>
</tr>
<tr>
<td>Magnetite</td>
<td>Fe(_3)O(_4)</td>
<td>0.01</td>
</tr>
<tr>
<td>Hematite</td>
<td>Fe(_2)O(_3)</td>
<td>0.01</td>
</tr>
<tr>
<td>Goethite</td>
<td>FeOOH</td>
<td>0.02</td>
</tr>
<tr>
<td>Ferrous hydroxide</td>
<td>Fe(OH)(_2)</td>
<td>0.02</td>
</tr>
<tr>
<td>Siderite</td>
<td>FeCO(_3)</td>
<td>0.02</td>
</tr>
<tr>
<td>Ferric hydroxide</td>
<td>Fe(OH)(_3)</td>
<td>0.02</td>
</tr>
</tbody>
</table>
Figure captions

**Figure 1:** Comparison of the evolution of porosity loss in a Fe$^0$ bed filled with spherical (left) and cylindrical (right) particles. The compactness is maximal for spherical particles. The roundness or sphericity of used materials (Fe$^0$ and additives) should be routinely characterized as this is crucial for the initial porosity.

**Figure 2:** Types of Fe$^0$-based filters for water treatment. The point O(0.0) represents a Fe$^0$ free filter (e.g. biosand filter, iron oxide-amended sand). The point I(100,100) correspond to a filter which is clogged just at Fe$^0$ depletion.

**Figure 3:** Evolution of the residual porosity as function of the volumetric proportion of Fe$^0$ is the filter for the two extreme values of the initial porosity ($\Phi_0 = 0.36$ and 0.62). It is seen that for $\Phi_0 = 0.36$ no filter is sustainable. For $\Phi_0 = 0.62$, filter operating under strictly anoxic conditions are sustainable.