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 (Fe^0) 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 Fe^0 barrier operation compared to contemporary theory. In the current work, a critical review of the physical chemistry of aqueous Fe^0 corrosion in porous media is presented. Subsequent implications for the design of Fe^0 filtration systems are modelled. The results suggest that: (i) for the pH range of natural waters (> 4.5), the high volumetric expansion of Fe^0 during oxidation and precipitation dictates that Fe^0 should be mixed with a non-expansive material; (ii) naturally-occurring solute precipitates have a negligible impact on permeability loss compared to Fe^0 expansive corrosion; and (iii) the proliferation of H_2 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^0 PRB system as a physical (size-exclusion) water filter device.

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

Acronym List

ITRC	Interstate Technology & Regulatory Council
PRB	Permeable reactive barrier
RZ	Reactive Zone
ZVI	Zerovalent iron

1 Introduction

Permeable reactive barriers containing metallic iron as a reactive filler material (Fe^0 PRBs) is an established technology for groundwater remediation [1-10]. At present, more than 120 Fe^0 PRBs have been installed worldwide, and effective performance has typically been reported [10-13]. Fe^0 PRBs typically contain either pure Fe^0 or a mixture of Fe^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^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^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_2O_3, Fe_3O_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 (ρ), and chemical composition (C) and mass fluxes (m) into or out of a system [39]:

$$V_p\rho_pC_{j,p}/100 + m_{j,flux} = V_w\rho_wC_{j,w}/100 \quad (1)$$

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 in cm^3), dry bulk density (ρ in g/cm^3), and elemental concentration (C in weight %). The mass of element j introduced into or out of the considered volume is indicated as $m_{j,flux}$ and is added to the mass of j in the system. Fluxes ($m_{j,flux}$) 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 = Fe) which is distributed between the original metallic iron (Fe^0 = ZVI) and various iron hydroxides and oxides (w = ox). Eq. 1 can therefore be written as:

$$V_{ZVI}\rho_{ZVI}C_{Fe,ZVI} + m_{Fe,flux} = V_{ox}\rho_{ox}C_{Fe,ox} \quad (2)$$

For pH > 4.5 the solubility of iron is very low and the flux of Fe ($m_{Fe,flux}$) 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:

$$V_{ZVI}\rho_{ZVI}C_{Fe,ZVI} = V_{ox}\rho_{ox}C_{Fe,ox} \quad (2a)$$

Eq. 2a suggests that V_{ox} (iron oxide) must be larger than V_{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, ε, the ratio of volume change in a process to the initial volume (Eq. 3):

$$\varepsilon = (V_{ox} - V_{ZVI})/V_{ZVI} = (V_{ox}/V_{ZVI}) - 1 \quad (3)$$

Eq. 3 suggests that the volumetric strain is positive because $V_{ox}/V_{ZVI} \geq 2.1$ [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_2O 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_2O 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 Φ_0 and the volume of pore is $Vp = \Phi_0*V_{rz}$. 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 (Φ_0) of 0.62. $\Phi_0 = 0.62$ is also from ref. [11].

130 The challenge of the current work is to evaluate which quantity of each fouling species (iron
131 corrosion products) is necessary to occupy the initial pore volume (Vp).

132 **3.1 Filling the pore volume with individual minerals and H_2 gas**

133 In this section, Eq. (4) assumes that Fe^0 is oxidized by water. The initial pore volume (Vp) is
134 filled entirely by corrosion products (H_2 and Fe^{II}/Fe^{III} species):

135 $$x\ Fe^0 + y\ H_2O \Rightarrow Fe_xO_y + y\ H_2\uparrow \qquad (4)$$

136	$t_0 = 0$	n_0	0	0
137	$t > t_0$	$n_0*(1 - \alpha)$	$n_0*\alpha/x$	$y*n_0*\alpha/x$
138	$t > t_0$	$x*n'_0*(1 - \alpha)$	$\alpha*n'_0$	$y*n'_0*\alpha$

139 It is considered that the number of moles (n_0) of Fe^0 at time t = 0 (t_0) is a multiple of n'_0 (n_0 =
140 $x*n'_0$). Accordingly, at t_0, the reactive zone contains only $x*n'_0$ Fe^0 (no oxide and no
141 hydrogen). At each time t ($t > t_0$), the residual number of moles of Fe^0 is $x*n'_0*(1 - \alpha)$, the
142 number of mole of generated oxide is $\alpha*n_0/x = \alpha*n'_0$ and the number of mole of H_2 is
143 $y*n_0*\alpha/x = y*n'_0*\alpha$ where α is the fraction of the initial amount of Fe^0 which is depleted as a
144 function of time (t). For iron hydroxides ($Fe(OH)_n$) and carbonate ($FeCO_3$), the stoichiometry
145 of oxygen is taken as the value of "x" (y = x) because each mole of Fe releases one mole of
146 H_2 (for n = 2).

147 Knowing the molar volume of individual oxides and H_2 (Tab. 1), the degree of occupation of
148 the initial pore volume (Vp) can be evaluated. The reactive zone is clogged when enough
149 corrosion products (Fe_xO_y and H_2) are produced to completely fill Vp. In other words, bed
150 clogging corresponds to Eq. (5):

151 $$V_{ZVI} + V_{ox} + V_{H2} = V_{rz} \qquad (5)$$

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

154 $$V_{m,ZVI}*x*n'_0(1 - \alpha) + V_{m,ox}*n'_0*\alpha + V_{m,H2}*n'_0*y*\alpha = V_{rz} \qquad (5a)$$

To have α values for individual oxides, it is sufficient to solve Eq. 5a. The solution is given by Eq. 5b:

$$\alpha = [V_{rz}/x*n'_0 - V_{m,ZVI}] / [V_{m,ox}/x + y/x*V_{m,H2} - V_{m,ZVI}] \quad (5b)$$

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 Φ ($V_{Fe}= C*V_{RZ} = (1-\Phi)* V_{RZ}$). 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 %). Φ_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 (Φ_0 = 36 %) and 24.6 (Φ_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 ($\Phi_{t\infty}$ = 0 %) when the initial porosity is 36 %. For Φ_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 (Φ_0).

The results herein suggest that, for Φ_0 = 36 %, when the main corrosion product is Fe_3O_4, only 58 % of Fe^0 is consumed just at system clogging. This value in agreement with the value

180 of 51 % reported in former works [38]. The difference corresponds to different values used
181 for the volumetric expansion coefficient (η); η = 1.97 herein vs. η = 2.08 in ref. [37].
182 However, this approach fails to consider the in-situ generation of colloidal Fe^{II}/Fe^{III} species
183 and their further transformation to hydroxides and oxides [44,45].
184 Eq. 5b describes a pure iron bed (100 % Fe^0). In the case that Fe^0 is admixed with a non
185 expansive additive (e.g. gravel, pumice, sand) the initial number of moles of iron (n_0) has to
186 be corrected to the fraction of n_0 corresponding to the volumetric proportion of Fe in the
187 reactive zone, e.g. $n_0/2$ for a system containing 50 % Fe^0 (v/v) and the balance amount of a
188 non porous material.
189 The results from Tab. 2 suggest that, at Φ_0 = 36 %, pure Fe^0 beds are not sustainable as a rule
190 (see section 3.2.2). For larger initial porosity (Φ_0), more sustainable systems are obtained.
191 This result was already theoretically achieved by admixing Fe^0 and porous media (e.g.
192 pumice). However, increased initial porosity as discussed here results from the geometry
193 (size, shape) of used media (e.g. Fe^0, sand, gravel).
194 The influence of the shape of the Fe^0 particles on the Fe^0 bed porosity is schematically
195 represented in Fig. 1 as spherical (left) and cylindrical (right) Fe^0 particles (black) are
196 progressively transformed to oxides (grey - rust). Fig. 1 confirms the fact that packed beds of
197 spherical media are the most compact [46-49]. This delineates the importance of
198 characterizing Fe^0 and sand materials for their uniformity and sphericity and the resulting bed
199 for its compactness (porosity).
200 Another important feature seen in Tab. 2 (α and α' values) is that regardless from the
201 abundance of Fe^0 in the system, bed clogging due to H_2 gas production is likely to occur prior
202 to the consumption of 0.1 % Fe^0. However, under the experimental conditions considered by
203 Henderson and Demond [11], gas accumulation is unlikely since the solutions were pumped
204 in upflow at a flow rate of 0.7 mL/min into the columns. In addition, under field conditions,

H_2 consuming bacteria are ubiquitous [29]. In such cases, clogging is therefore more likely to result from enhanced (bio-)stimulation (biofilm growth) and not from H_2 accumulation.

The estimations in this section clearly show that if H_2 was primarily responsible for bed clogging, then it is unlikely that the Fe^0 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 Fe^0 had corroded. However, H_2 gas may contribute to permeability loss in association with particle 'cementation' (compaction) by nascent iron hydroxides. In this case, compaction prohibits H_2 escape and increases flow resistance for pumped solutions.

3.2 The process of permeability loss in Fe^0/H_2O systems

In this section, a contemporary evaluation of permeability loss in the Fe^0/H_2O system is given. The methodology is explicitly presented in ref. [38]. In the current work the following assumptions apply:

(i) Uniform Fe^0 corrosion: the radius reduction of spherical or cylindrical Fe^0 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) Fe^0 corrosion products are fluid enough to progressively fill available pore space.

As shown in section 2.3, iron corrosion occurs with concurrent volumetric expansion ($\eta = V_{ox}/V_{ZVI} > 1$). The excess volume of Fe^0 imbued by corrosion product formation is given by V_{excess} in Eq. 6. By definition, V_{excess} is the difference between V_{ox} and V_{ZVI} (Eq. 6).

$$V_{excess} = (\eta - 1) * V_{ZVI} \quad (6)$$

The Fe^0 filtration system is clogged when the volume V_{excess} is equal to the initial inter granular voids (Vp). "V_{ZVI}" in Eq. 6 represents the volume of Fe^0 in a pure Fe^0 bed. However, as discussed in sections 1 and 3.1, Fe^0 should be only a fraction of V_{solid} ($V_{ZVI} = \tau_{ZVI} * V_{solid}$, with $\tau_{ZVI} \leq 1$). Eq. 6 can be rewritten as:

231 $$(\eta - 1) * \tau_{ZVI} * V_{solid} = V_{excess} \quad (6a)$$

232 Eq. 6a suggests that, for every η value (i.e. every oxide), V_{excess} is a linear function of τ_{ZVI}. To
233 find out at what extent τ_{ZVI} contributes to complete pore filling, it is sufficient to graphically
234 solve Eq. 6a for $V_{excess} = V_P$. Practically, there are two equivalent approaches: (i) solving
235 $V_{excess} - Vp = 0$ or (ii) solving $V_{excess}/V_P = 1$. The second approach is adopted in this work.
236 The solution of Eq. 6a (clogging) is the interception of the line $V_{excess}/V_P = f(\tau_{ZVI})$ with the line
237 100 % (Fig. 2). Before discussing the actual evolution of the porosity, some fundamental
238 aspects for the solution of Eq. 6a will be given.

239 **3.2.1 Fe^0 filtration systems**

240 To date, Fe^0 particles have been widely reported as successful for water treatment [50-53].
241 However, a holistic understanding of the Fe^0/H_2O system is yet to be achieved.

242 Fig. 2 represents the principle of Fe^0 filtration beds. The origin (point O) represent a Fe^0-free
243 filter (e.g. activated alumina, activated carbon, gravel, pumice, sand, zeolite) and point
244 I(100,100) represents an "ideal Fe^0-based filter" which becomes 100 % clogged concurrent
245 with 100 % Fe^0 depletion ($V_{excess}/V_P = 1$). The line OI divides the graph into two halves.
246 Below OI, $V_{excess}/V_P < 100$ and the system is not clogged at Fe^0 depletion. Above OI,
247 $V_{excess}/V_P > 100$ and the system is clogged before Fe^0 depletion (a proportion of Fe^0 is
248 wasted). Thus, Fig. 2 can be regarded as a useful reference tool for future work within this
249 field. Relevant parameters to complement Fig. 2 that will be investigated in future work
250 include: (i) the intrinsic reactivity of Fe^0; (ii) the shape and size of Fe^0; (iii) the shape and size
251 of sand; (iv) the dimensions and the geometry of the Fe^0 bed; (v) the thickness of the Fe^0/sand
252 layer; (vi) the proportion of Fe^0 in the Fe^0/sand layer; and (vii) the water flow velocity.

253 Point O in Fig. 2 represents all filtration designs without Fe^0 (or another metallic element).
254 These include conventional slow sand filters (SSF), biosand filters (BSF) and iron oxide-
255 coated sand filters. Considering filtration designs which entirely contain sandy materials,
256 point O can be limited to BSF and SSF. SSF have been used for water treatment since 1840 in

257 Dijon/France by Henry Darcy [54]. BSF have been used for water treatment at household
258 level for over 20 years [55,56]. However, despite intensive research on BSF, their operating
259 mode is yet to be completely understood [42,43,55]. For example, there are no established
260 comprehensive design criteria for BSF [41,55,57]. Accordingly, the reproducibility and
261 comparison of reported results from one setting to another is problematic. To fill this gap,
262 Kubare and Haarhoff [41] have provided the most recent systematic review for a rational
263 design of BSF. A Fe^0 filtration system (Fig. 2) can be regarded as a modification of a SSF or
264 BSF (point O). Therefore, it is essential to carefully develop rational and comprehensive
265 engineering design criteria. In this effort, designing tools for BSF would be very helpful
266 [41,55].

267 **3.2.2 The role of initial porosity in Fe^0 bed clogging**

268 The theoretical discussion of Fe^0 PRB porosity until now was focused on the case of
269 maximum compactness for which the initial porosity is 0.36 (Φ_0 = 36 %) [32]. For such
270 systems, a pure Fe^0 bed is clogged when less than 60 % of the initial amount of Fe^0 is
271 depleted (section 3.1). According to Fig. 1, for Φ_0 = 36 %, all Fe^0 beds are situated above line
272 OI. However, significantly larger porosity values have typically been reported in the
273 literature, the highest being 62 % by Henderson and Demond [11]. Accordingly, this section
274 discusses the evolution of the porosity of a conventional sand filter (0 % Fe^0) as it is
275 progressively transformed to a pure Fe^0 filter (100 % Fe^0). Particular attention is paid to the
276 extreme values of the porosity (Φ_0 = 36 and 62 %). The results are summarized in Fig. 3.

277 The ideal line OI is not represented in Fig. 3 for clarity. Instead the point I(100,100) is
278 represented. Fig. 3a (Φ_0 = 0.36) shows clearly that all systems are clogged before Fe^0
279 depletion has been occurred. In contrast, Fig. 3b shows that, for an initial porosity (Φ_0) of
280 0.62, Fe^0 beds are sustainable if magnetite (Fe_3O_4), maghemite (γ-Fe_2O_3) and hematite
281 (Fe_2O_3) are the sole iron corrosion products. Additionally, it shows that ferrous hydroxide
282 ($Fe(OH)_2$) is the "ideal corrosion product" for the Fe^0 PRB to clog concurrent with Fe^0

283 depletion. With the formation of ferrous hydroxide, magnetite, maghemite and hematite being
284 more prevalent in anoxic conditions, it can therefore be stated that Fe^0 PRBs are most ideally
285 suited for oxygen depleted or anoxic conditions.
286 Magnetite (x_{Fe} = 72.4 %, Tab.1) may result from $Fe(OH)_2$ dehydration under anoxic
287 conditions and is therefore the sole mineral, that is likely to be quantitatively generated from
288 anoxic Fe^0 corrosion.
289 **3.2.3 Discussion**
290 The presentation until now has focused on the evolution of the permeability loss as a key
291 factor for the sustainability of Fe^0 PRB systems. A Fe^0 filtration system is sustainable only if
292 it can maintain hydraulic (permeability) performance while also remaining effective for
293 pollutant removal. In other words, a permeable but non reactive Fe^0 filtration system is
294 useless.
295 A Fe^0 filtration system can be considered both a chemical and physical water filter device,
296 with its efficacy dictated by progressive expansion/compression cycles during aqueous
297 corrosion [52]. In a Fe^0 filtration system, chemical reactions included (i) iron oxidative
298 dissolution, (ii) polymerisation of iron hydroxides and, (iii) subsequent precipitation of
299 hydroxides and oxides. Quantitative chemical transformations (oxidation/reduction) of
300 dissolved species may also occur. However, resulted species must be removed from the
301 aqueous phase by a physical process: adsorption, occlusion, size-exclusion. Accordingly, Fe^0
302 is not a strong reducing agent under environmental conditions as widely accepted [5-7,10].
303 More importantly, reduction is not a stand alone contaminant removal mechanism [58-61].
304 Rather, Fe^0 is a generator of contaminant scavengers for reactive filtration [44,62-65]. While
305 adsorptive filtration has been mostly used for metal removal [62-65], the affinity of organic
306 compounds for iron hydroxide/oxides (corrosion products) is well documented [66-71]. For
307 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.

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553 **Table 1**: Some characteristics of metallic iron (Fe^0) and its main corrosion products
554 commonly identified in Fe^0 PRBs. "x" is the weight percent of Fe in the phase. As a
555 rule, oxides formed under anoxic conditions exhibit larger x values. "η" is the
556 calculated coefficient of volumetric expansion. Phase parameters are compiled from
557 Balasubramaniam et al. [40] and Henderson and Demond [11].
558

Phase	**Name**	**Structure**	**Density** (g/cm^3)	**V_m** (cm^3/mol)	**x** (%)	**η** (-)
Fe^0	Iron metal	bcc	7.86	7.6	100.0	-
$Fe(OH)_3$	Fe^{III} hydroxide	perovskite-like	3.1	34.4	52.0	4.53
$FeCO_3$	Siderite	Trigonal	3.83	29.3	48.3	3.86
$Fe(OH)_2$	Fe^{II} hydroxide	Trigonal	3.4	26.4	62.2	3.47
α-FeOOH	Goethite	Orthorhombic	4.28	20.3	62.9	2.67
γ-Fe_2O_3	Maghemite	Cubic	4.69	29.1	70.0	1.91
α-Fe_2O_3	Hematite	Trigonal	5.3	30.1	70.0	1.98
Fe_3O_4	Magnetite	Cubic	5.175	45.0	72.4	1.97

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561 **Table 2**: Estimation of the extent of Fe^0 depletion (α value in %) in the column of Henderson
562 and Demond [11] for two values of the initial bed porosity. α and α_1 correspond to $\Phi_0 = 36$ %
563 when H_2 remains in the system or escapes respectively and α' and α'_1 correspond to $\Phi_0 = 62$
564 % when H_2 remains in the system or escapes respectively. It is seen that in all cases the initial
565 porosity is filled by gas when less than 0.1 % of the initial mass of Fe^0 is corroded. A value of
566 100 % is related to a system which is not clogged when Fe^0 is depleted.
567
568

Name	**Formula**	**α values** (%)			
		α	α_1	α'	α'_1
Maghemite	Fe_2O_3	0.01	62	0.04	100
Magnetite	Fe_3O_4	0.01	58	0.04	100
Hematite	Fe_2O_3	0.01	57	0.04	100
Goethite	FeOOH	0.02	34	0.06	98
Ferrous hydroxide	$Fe(OH)_2$	0.02	24	0.06	70
Siderite	$FeCO_3$	0.02	20	0.06	57
Ferric hydroxide	$Fe(OH)_3$	0.02	16	0.06	46

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570 **Figure captions**

571

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

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

579 **Figure 3**: Evolution of the residual porosity as function of the volumetric proportion of Fe^0 is
580 the filter for the two extreme values of the initial porosity (Φ_0 = 0.36 and 0.62). It is
581 seen that for Φ_0 = 0.36 no filter is sustainable. For Φ_0 = 0.62, filter operating under
582 strictly anoxic conditions are sustainable.