

1 **Effect of pumice and sand on the sustainability of granular iron beds for the**
2 **aqueous removal of Cu^{II}, Ni^{II}, and Zn^{II}**

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10
11 **Running Title:** Admixing pumice and sand to reactive Fe⁰ sustains long-term metal removal.

12
13 **Acronym List**

14 PRB Permeable Reactive Barrier

15
16 **Keywords:** Hydraulic conductivity, Reactive barriers, Pumice, Sand, Zerovalent iron.

18 **Abstract**

19 Current knowledge of the basic principles underlying the design of Fe⁰ beds is weak. The
20 volumetric expansive nature of iron corrosion was identified as the major factor determining the
21 sustainability of Fe⁰ beds. This work attempts to systematically verify developed concepts. Pumice
22 and sand were admixed to 200 g of Fe⁰ in column studies (50:50 volumetric proportion). Reference
23 systems containing 100 % of each material have been also investigated. The mean grain size of the
24 used materials (in mm) were 0.28 (sand), 0.30 (pumice) and 0.50 (Fe⁰). The five studied systems
25 were characterized (i) by the time dependent evolution of their hydraulic conductivity
26 (permeability) and (ii) for their efficiency for aqueous removal of Cu^{II}, Ni^{II}, and Zn^{II} (about 0.30 M
27 of each). Results showed unequivocally that (i) quantitative contaminant removal was coupled to
28 the presence of Fe⁰, (ii) additive admixture lengthened the service life of Fe⁰ beds, and (iii) pumice
29 was the best admixing agent for sustaining permeability while the Fe⁰/sand column was the most
30 efficient for contaminant removal. The evolution of the permeability was well-fitted by the
31 approach that the inflowing solution contained dissolved O₂. The achieved results are regarded as
32 starting point for a systematic research to optimise/support Fe⁰ filter design.

33 **1 Introduction**

34 Permeable reactive barriers (PRBs) containing metallic iron (Fe⁰) as reactive medium have been
35 developed during the past two decades to an established technology for groundwater remediation
36 [1-11]. The original PRB technology containing granular Fe⁰ has been expanded to the injection of
37 nano-scale Fe⁰ for source remediation [8-11]. To date, more than 180 Fe⁰ PRBs have been installed
38 worldwide [8,11]. Successful accomplishment of remedial goals has been typically reported. At
39 some few sites, system failures were recorded [8,12]. Reported failures were attributed to design
40 shortcomings due to poor site characterization (reason 1), poor design selection (reason 2) or
41 installation at sites where the technology is not an appropriate choice (reason 3) [8,12,13].
42 However, there is clear evidence that the physico-chemistry of the Fe⁰/H₂O system was not properly

43 considered [14]. Accordingly, design shortcomings may have reasons different from or additional to
44 reasons 1, 2 and 3.

45 A major concern of Fe⁰ PRBs is related to the reduction of the hydraulic conductivity (permeability
46 loss) with time [15-17]. Laboratory and field data have also demonstrated diminished Fe⁰ reactivity
47 with time [9, 18]. Consequently, the sustainability of Fe⁰ PRBs in terms of both Fe⁰ reactivity and
48 system permeability has been extensively discussed during the past 15 years [1,18-24]. Reported
49 results are confusing and even conflicting as demonstrated below for trichloroethene (TCE).

50 O'Hannesin and Gillham [1] reported on successful TCE (268 mg/L) reductive degradation by a
51 Fe⁰/sand mixture containing 22 % Fe⁰ by weight (laboratory and field test). Bi et al. [21] tested
52 several weight Fe⁰/sand mixtures (25/75, 50/50, 75/25, 85/15 and 100/0) for TCE (up to 60 mg/L)
53 treatment and reported that the system with less than 50 % Fe⁰ was not efficient (laboratory test).
54 Ruhl et al. [18] evaluated four dual mixtures (Fe⁰/anthracite, Fe⁰/gravel, Fe⁰/pumice and Fe⁰/sand)
55 for TCE (about 10 mg/L) treatment (laboratory test). The used masses of additives varied from 24.4
56 g for pumice to 104.3 g for gravel. The used mass of Fe⁰ was 100 g resulting in Fe⁰ weight ratios
57 varying from 49 % for gravel to 80 % for pumice. Ruhl et al. [18] concluded that tested dual
58 systems are not applicable for TCE treatment but "might be applicable for the removal of heavy
59 metals".

60 The three examples reveal that researchers use varying experimental procedures to characterize
61 processes in Fe⁰/H₂O systems (see Tab. 1) [1,21,25-33]. These procedures differ for instance in Fe⁰
62 intrinsic reactivity, Fe⁰ pre-treatment, Fe⁰ mass, Fe⁰ particle size and shape, used admixing
63 additives and their proportions, duration of the experiments, nature and concentration of the
64 contaminant, buffer application, solution flow velocity and water chemistry. As a result, many
65 different reports for the same compound are available in the literature (even for the same Fe⁰).

66 Water and dissolved inorganic constituents (Ca²⁺, HCO₃⁻, Mg²⁺, O₂, PO₄³⁻, SO₄²⁻) react with iron
67 species (Fe⁰, Fe^{II} and Fe^{III}) to form precipitates that progressively fill the inter-particle porosity

68 within a Fe^0 filter. The potential of these in situ generated precipitates to limit the permeability and
69 the efficiency of Fe^0 PRBs filters has been clearly documented [1,4,6-8]. However, the role of Fe^0
70 oxidation by water has not always been properly considered and the role of gas (H_2) formation in
71 porosity/permeability loss has been sometimes overestimated [15,16]. Recent theoretical works
72 demonstrated that a Fe^0 -based filter should be considered as a system in which iron is corroded
73 mostly by water and the micro-pollutants are sequestered in the matrix of precipitation corrosion
74 products [14,34-36]. This view corroborates concordant reports regarding Fe^0 filters as a long-term
75 sink for C, S, Ca, Si, Mg, and N [12,37-39].

76 The present work is an attempt to improve the design of Fe^0 filtration systems based on recent
77 theoretical studies [14]. In the present work, the efficiency of five different systems (A to E) for
78 aqueous contaminant removal is tested in column studies. The volumetric composition of individual
79 systems is given as: (A) 100 % sand, (B) 100 % pumice, (C) 100 % Fe^0 , (D) 50:50 Fe^0 :pumice, and
80 (E) 50:50 Fe^0 :sand. The model solution contained about 0.30 M of Cu^{II} , Ni^{II} , and Zn^{II} . The
81 evolution of the systems is characterized by determining the (i) extend of contaminant removal, and
82 (ii) evolution of hydraulic conductivity.

83 **2 Materials and methods**

84 **2.1 Chemicals and solutions**

85 Copper(II) nitrate hydrate (purity 99.999), nickel(II) nitrate hexahydrate (purity 99.999) and zinc(II)
86 nitrate hexahydrate (purity 99.000) were obtained from Sigma-Aldrich. All chemicals used for
87 experiments and analysis were of analytical grade. The used solutions were obtained by dissolving
88 copper nitrate, nickel nitrate and zinc nitrate in distilled water. The molar concentration of the
89 resulting solution was as follows: 0.27 M Cu, 0.29 M Ni and 0.37 M Zn. The corresponding mass
90 concentrations are 17 mg/L Cu, 17 mg/L Ni, and 23 mg/L Zn.

91 **2.2 Solid materials**

92 **2.2.1 Porosity of binary granular media**

93 The total porosity Φ of a binary granular medium composed of two kinds of particles P1 and P2
 94 (here P1 corresponds to Fe^0 particles) is given by :

$$\Phi = \Phi_{\text{inter}} + \varphi_{\text{pp}} \cdot f_{\text{pp}} = \left[1 - \frac{V_{a1} + V_{a2}}{V_{\text{rz}}}\right] + \varphi_2 \cdot \frac{V_{a2}}{V_{\text{rz}}}$$

$$\Phi = \left[1 - \frac{M_1/\rho_{\text{sa1}} + M_2/\rho_{\text{sa2}}}{V_{\text{rz}}}\right] + \varphi_2 \cdot \frac{M_2/\rho_{\text{sa2}}}{V_{\text{rz}}} \quad (1)$$

96 Where: (i) Φ_{inter} is inter-particle porosity (ii) V_{ai} , M_{ai} , ρ_{ai} are respectively the apparent volume of
 97 the particles i , the mass and the apparent specific weight, and φ_2 is the intra-particle porosity of
 98 the particles 2 with $\varphi_2 = 0$ for non porous particles (sand) and $\varphi_2 \neq 0$ for porous particles (pumice)
 99 and (iii) V_{rz} is the total packing volume of the granular medium.

100 2.2.2 Metallic iron (Fe^0)

101 The used Fe^0 is of the type FERBLAST RI 850/3.5, distributed by Pometon S.p.A., Mestre - Italy.
 102 The powdered material contains mainly iron (> 99.74 %). Identified impurities include mainly Mn
 103 (0.26 %), O, S and C. The material is characterized by uniform grain size distribution. The
 104 coefficient of uniformity U (ratio between the diameters corresponding to 60 and 10 % finer in the
 105 grain size distribution) is 2. The mean grain size (d_{50}) is about 0.5 mm and the initial porosity of
 106 used Fe^0 medium has been estimated to be $\Phi_0 = 49.6$ % (see Tab. 2, Eq. 1).

107 2.2.3 Pumice

108 The used pumice originates from Lipari (Aeolian Islands, Sicily – Italy). Its mineralogical
 109 composition was determined as follows: SiO_2 : 71.75 %; Al_2O_3 : 12.33 %; K_2O : 4.47 %; Na_2O : 3.59
 110 %; Fe_2O_3 : 1.98 %; moreover it contains about 4 % of bound water entrapped in the pumice structure
 111 during the sudden cooling of magma and traces of other compounds (e.g. CaO , SO_3 , MgO , TiO_2 ,
 112 FeO , MnO , P_2O_5). The material is characterized by uniform grain size distribution. The coefficient
 113 of uniformity U is 1.4. The mean grain size (d_{50}) is about 0.3 mm. This type of pumice has been
 114 chosen since it was the available fraction closest to Fe^0 in dimension. The initial porosity of the

115 pumice granular medium has been estimated to be $\Phi_0 = 73.3 \%$ and the inner porosity of the pumice
116 (intra particular porosity ϕ_{pp}) to be 41 % (Tab. 2, Eq. 1) through Mercury Intrusion Porosity (MIP)
117 measurements under the hypothesis that the relative density (packing) of granular mixtures in the
118 columns and during MIP experiments were the same.

119 **2.2.4 Sand**

120 The used quartz sand was obtained from a river quarry. The sand was carefully washed with
121 distilled water and sieved before use. The material is characterized by uniform grain size
122 distribution. The coefficient of uniformity U is 2.2. The mean grain size (d_{50}) is about 0.28 mm. The
123 material was used without any further characterization. The initial porosity of the sand medium has
124 been estimated to be $\Phi_0 = 45.0 \%$ (Tab. 2, Eq. 1).

125 **2.3 Column operation**

126 Laboratory scale polymethyl methacrylate (Plexiglas) columns were operated in up-flow mode. The
127 influent solution was pumped upwards from a single PE bottle using a precision peristaltic pump
128 (Ismatec, ISM930). The flow rate was maintained constant at a value of 0.5 mL/min. Tygon tubes
129 were used to connect inlet reservoir, pump, columns and outlet. Five plexiglas columns (50 cm
130 long, 5.0 cm inner diameter) were used in the experiments (Fig. 1).

131 Five different systems were investigated (Systems A through E) (Tab. 3). System A was the
132 operational reference system containing only sand (0 % Fe^0), System B was the second operational
133 reference containing only pumice (0 % Fe^0) and system C was a pure iron bed (100 % Fe^0). The
134 volumetric proportion of Fe^0 in the 2 other systems (D, E) was 50 %. In systems C to E, the mass of
135 iron was fixed to 200 g. This mass represented either 100 % of the reactive zone (rz) or the relevant
136 volumetric proportion of rz (Fig. 1, Tab. 3). In system B the pumice volume was set to be the same
137 occupied by Fe^0 in system C while the pumice mass was obviously the same as in system E. The
138 total porosity of the all systems varies between 45 % and 73 % (Tab. 2, Eq. 1).

139 The hydraulic conductivity [40] was determined during the column tests, by either constant-head (k
140 $> 10^{-6}$ m/s) or variable-head ($k < 10^{-6}$ m/s) permeability methods, at selected dates to assess the
141 permeability of the systems. The experiments were performed at room temperature (21 ± 4 °C).
142 Samples for analysis were collected at periodic intervals and the experiments were prolonged until
143 contaminant breakthrough (systems A and B) or a significant loss of the hydraulic conductivity
144 (systems C to E) was observed.

145 **2.4 Analytical methods**

146 Samples from the columns were centrifuged at 3000 rpm (ALC, PK121 Multispeed Centrifuge).
147 The supernatant was vacuum filtered through a 0.45 μm glass filters. The aqueous concentrations of
148 Cu, Fe, Ni and Zn were then measured by Atomic Absorption Spectrophotometry (AAS - Shimadzu
149 AA – 6701F; wavelengths: Cu 324.75 nm, Ni 232.00 nm, Zn 213.86 nm, Fe 248.33 nm) using air-
150 acetylene flame and according to conventional Standard Methods [41]. The used AAS device was
151 calibrated using three operational standard solutions covering the expected concentration range of
152 the samples (after dilution if applicable). Each operational standard solution was prepared by an
153 appropriate dilution of a 1000 ppm ($\text{Cu}(\text{NO}_3)_2$, $\text{Fe}(\text{NO}_3)_3$, $\text{Ni}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2$) certified atomic
154 absorption stock solution from Merck (Germany). The minimum correlation coefficient of
155 calibration curves was of 0.997. The pH value was measured by combination glass electrodes
156 (WTW GmbH, inolab pH/Cond 720).

157 **2.4.1 MIP measurements**

158 MIP measurements have been carried out using a Micromeritics instrument apparatus type
159 (AutoPore IV 9500). The instrument is capable of a minimum intruding pressure of 3.4 kPa and a
160 maximum pressure of 227 MPa, so that the pore radius ranges from 2.7 nm to 180 μm .

161 For pumice particles the measured pore data allow determining the inter-particle and intra-
162 particle porosities of the pumice particles, the apparent specific weight ρ_{as} (defined as the ratio of
163 the mass and the apparent volume of the pumice particles) and the specific weight ρ_{s} (defined as the

164 ratio of the mass and the volume of the solid phase of the pumice particles).

165 **2.5 Expression of the experimental results**

166 In order to characterize the magnitude of tested systems for contaminant removal, the removal
167 efficiency (E) and the specific removal (E_s) were calculated using Eq. 2 and Eq. 3 [33].

$$168 \quad E = m_{\text{rem}}/m_{\text{in}}*100 \quad (2)$$

$$169 \quad E_s = m_{\text{rem}}/m_{\text{Fe}}*100 \quad (3)$$

170 where m_{in} is the mass of contaminant flowed into the column, m_{rem} is the mass of removed
171 contaminant, and m_{Fe} the mass of Fe^0 present in the column.

172 **2.6 Evaluation of the residual porosity**

173 When iron corrodes, porous oxide layers are formed at the $\text{Fe}^0/\text{H}_2\text{O}$ interface. The volume of the
174 corrosion product (V_{oxide}) is higher than that of the original metal (V_{Fe}). The ratio (η) between the
175 volume of expansive corrosion product and the volume of iron consumed in the corrosion process is
176 called ‘‘coefficient of volumetric expansion’’ [42,43]. Generally, V_{oxide} is 2.08 to 6.40 times larger
177 than V_0 ($2.08 \leq \eta \leq 6.40$ for free expansion).

178 At any time ($t > 0$), V_{oxide} can be calculated using Eq. 4:

$$179 \quad V_{\text{oxide}} = \eta*(V_0 - V_t) \quad (4)$$

180 Where η is the coefficient of volumetric expansion, $(V_0 - V_t)$ is the consumed Fe^0 volume with V_0
181 the initial volume of Fe^0 and V_t its residual Fe^0 at time t .

182 The effective volumetric expansion ΔV (Eq. 5) corresponding to the volume of pores that is
183 occupied by iron corrosion products is a measure of the extent of porosity loss.

$$184 \quad \Delta V = (\eta - 1)*(V_0 - V_t) \quad (5)$$

185 The residual porosity of the system at time t ($\Phi(t)$) may be estimated by (Eq. 6):

$$186 \quad \Phi(t) = \Phi_0 - \frac{(\eta - 1) \cdot (V_0 - V_t)}{V_{\text{rz}}} \quad (6)$$

187 Where Φ_0 is the initial porosity of the reactive zone given in Tab. 3, and V_{rz} is the volume of the

188 reactive zone.

189 **3 Results and discussion**

190 **3.1 pH variation and Fe breakthrough**

191 Metal ions are known to be removed from the aqueous phase in packed Fe^0 beds by adsorption, co-
192 precipitation and adsorptive size-exclusion when the $\text{pH} > 4.5$ [44-48]. Figure 2a clearly
193 demonstrates that the pH value of the initial solution ($t = 0$) and that of the effluent from all
194 columns was larger than 5.5. This suggests that contaminant removal could be quantitative (see Tab.
195 4) if the residence time is sufficient to enable the formation of enough iron corrosion products for
196 contaminant retention in the column. A hint that quantitative contaminant removal was likely is
197 given by the evolution of the iron concentration (Fig. 2b). Fig. 2b clearly shows that the effluent
198 iron concentration was less than 0.2 mg/L and reached values close to up to 1 mg/L only shortly
199 before clogging for the system with 50 % pumice (system E). This observation could be attributed
200 to accelerated transport through preferential flow paths [26].

201 **3.2 Metal breakthrough**

202 Fig. 3 and Tab. 4 summarize the results of contaminant removal in systems containing Fe^0 . It is
203 clear from Fig. 3a that no Cu breakthrough occurs. Ni breakthrough occurs first (Fig. 3b). In fact Ni
204 breakthrough occurs before day 8 in the system with 100 % Fe^0 . Zn is the next less retained metal
205 with a breakthrough occurring at day 10 in the system with 100 % Fe^0 (Fig. 3c). The observed order
206 of removal efficiency corresponds to the selectivity sequence for iron oxides and soils: $\text{Ni} < \text{Zn} <$
207 Cu [49-51]. For example, Fontes and Gomes [50] found that in competitive adsorption Cu^{II}
208 maintains its strong affinity with the surface, while Ni^{II} and Zn^{II} are displaced from the surface. This
209 observation corroborates the view that species with higher affinity to iron oxides are better treated
210 by Fe^0 filters [23,24,52,53].

211 Another important result from Fig. 3 is that no contaminant breakthrough was observed in the
212 system with 50 % sand (system D). This system is less porous than the system with 50 % pumice

213 (Tab. 3). The differential behaviour of the systems with pumice and sand (D and E) illustrates the
214 dilemma of sustaining efficiency (maximum Fe^0 ratio) while maintaining permeability, for instance
215 by using porous pumice in place of sand [33]. As discussed in details elsewhere [14,36] this
216 dilemma could be solved by using an appropriate thickness of the Fe^0 -based layer for each relevant
217 additive (e.g. activated carbon, anthracite, gravel, pumice, sand) to achieve water treatment under
218 site specific conditions. Relevant site specific parameters include the nature of contaminant, the
219 water chemistry and the water flow velocity. In other words, a proper design (reason 2, § 1) should
220 be extended to the width of the Fe^0 PRB, the nature of the admixing agent (e.g. type and grain size
221 distribution) and the proportion of Fe^0 therein.

222 The last important issue on contaminant breakthrough concerns the suitability of specific removal
223 (Eq. 3) for a dynamic system in which reactive species are progressively generated. E_s values from
224 Tab. 4 show that the lowest specific removal (1.74 mg Ni/g Fe^0) was obtained in system C (100 %
225 Fe^0). While this result seems contradictory, it corroborates the view that iron corrosion is self-
226 inhibitory and that decreasing the proportion of Fe^0 is a powerful tool to increase sustainability
227 ([54] and ref. cited therein). Tab. 5 shows that correcting E_s by considering the extent of Fe^0
228 depletion at t_{limit} ($E_{s,\text{eff}}$) restores the intuitive trend that “the greater the adsorbent amount, the larger
229 the E_s value“. Accordingly, the highest $E_{s,\text{eff}}$ values were obtained in system C (absolute value)
230 which clogged at first. This result corroborates previous findings that filtration systems containing a
231 100 % Fe^0 layer are efficient but not sustainable [55,56]. Moreover, the fact that the effective
232 specific removals for the three systems are similar ($4.0 \leq E_{s,\text{eff}} \leq 6.8$) is a hint that the calculation of
233 the consumed iron is right. Note that, $E_{s,\text{eff}}$ values are derived from E_s values on the basis of the
234 extent of Fe^0 depletion at t_{limit} (E_s, t_{limit}), not at the depletion at the end of the experiment. This result
235 means that no significant breakthrough was observed before t_{limit} .

236 3.3 Hydraulic conductivity

237 The results presented in Fig. 4 clearly demonstrate that the hydraulic conductivity decreases with
 238 time for the systems containing Fe⁰ particles (systems C, D, E) then remains constant at time t_{limit}
 239 (Tab. 5).

240 The initial hydraulic conductivity K₀ for all systems is about 5.10⁻⁴ m/s. The hydraulic conductivity
 241 tends to about the limit value K_{limit} = 5.10⁻⁹ m/s at time t_{limit}. The results show that the decrease of
 242 the permeability is down to about five orders of magnitude K₀/K_{limit} = 1.10⁻⁵ (-). The time t_{limit}
 243 seems to depend on the investigated system (Tab. 5). The data in Tab. 5 clearly indicate that Fe⁰
 244 admixture with sand and pumice resulted in extended service life. The longest service life was
 245 observed for the system with pumice particles and is consistent with the fact that intra-particle
 246 porosity has contributed to increased permeability [57,58].

247 Among the proposed models in the literature, the Kozeny-Carman equation is often considered to
 248 evaluate the evolution of the hydraulic conductivity [59]. This equation was developed after
 249 considering a porous material as an assembly of capillary tubes and yielded the hydraulic
 250 conductivity K as function of the porosity Φ, the specific surface S (m²/kg of solids) and a factor C
 251 to take into account the shape and tortuosity of channels. The first approximation is to accept the
 252 Kozeny-Carman equation [60-64]:

$$253 \quad K(t) = K_0 \cdot \left(\frac{\Phi}{\Phi_0}\right)^3 \cdot \left(\frac{1-\Phi_0}{1-\Phi}\right)^2 \quad (6)$$

254 where K₀ is the initial hydraulic conductivity and Φ₀ the initial porosity.

255 For the evaluation of the residual porosity Φ as a function of the time t, uniform corrosion for
 256 spherical particles with initial radius R₀ (here R₀ = 500 μm) is assumed. Individual particles corrode
 257 independently with the same kinetics until material depletion. Under these assumptions, it is
 258 considered that the actual radius R(t) of Fe⁰ particles varies linearly with time t according to:

$$259 \quad R(t) = R_0 - \frac{R_0 \cdot t}{t_{\infty, \text{depletion}}} \quad (7)$$

260 where $t_{\infty, \text{depletion}}$ is the time at Fe^0 depletion.

261 From Eq. 5, 6 and 7, it is possible to simulate the decrease of the hydraulic conductivity as a
262 function of time (Figure 4b-d). The modelling has been applied for the coefficient of volumetric
263 expansion $\eta = 6.40$ in coherence with high O_2 levels and for two times at Fe^0 depletion ($t_{\infty, \text{depletion}} =$
264 50 days and 62.5 days) [43]. It can be noticed that the maximum volume of Fe^0 which may corrode
265 is the one which leads to clogging ($V_{\text{Fe, clogging}}$) and is expressed by:

266
$$V_{\text{Fe, clogging}} = \frac{\Phi_0 \cdot V_{\text{rz}}}{\eta - 1}. \quad (8)$$

267 At time t_{limit} it is assumed that the volume of consumed Fe^0 tends to the one leading to the clogging
268 of the column ($V_t = 1.01 \cdot (V_0 - V_{\text{Fe, clogging}})$ in calculations) and remains constant for $t > t_{\text{limit}}$. Under
269 these assumptions, the permeability K_{limit} corresponding to the time t_{limit} is reached at the clogging
270 of the columns ($\Phi \approx 0$, see Tab. 5). The obtained results show that there is a good agreement
271 between experiment and modelling concerning the kinetic of the decrease of the permeability with
272 time and the K_{limit} value. It can be noticed that the linear law for corrosion process (Eq. 7) with the
273 two considered times ($t_{\infty, \text{depletion}}$) as a first approximation of corrosion kinetic, allows to well
274 reproduce the decrease of the permeability at the beginning of the filtration process. However, the
275 evolution of the permeability around t_{limit} can not be accurately predicted.

276 The proposed modelling is a first attempt to predict the time-dependent decrease of the hydraulic
277 conductivity (permeability loss) on the basis of the volumetric expansion of corroding iron. This
278 work shows that the evolution of the hydraulic conductivity may be predicted without considering
279 the evolution of the tortuosity or the specific surface in the Kozeny-Carman equation and is the
280 consequence of the filling of the porosity by expansive iron corrosion products.

281 **3.4 Discussion**

282 The achieved experimental results and the proposed modelling show that there is a significant effect
283 of the inner porosity of the pumice (system E). This effect is a clogging delay compared to the

284 Fe⁰/sand system (Fig. 4). This result is explained by the internal porosity of pumice particles which
285 may store iron corrosion products, delaying the filling of the inter-granular porosity. Although
286 theoretically sound [58,65,66], this hypothesis has to be confirmed in future works, for instance,
287 using X-ray micro-tomography to probe inner porosity of the pumice specimen and considering
288 various pumice material with differential pore connectivity.

289 For a better understanding of the evolution of the initial porosity as iron corrosion proceeds, it is
290 imperative to couple imaging (visualization) and mathematical modelling. The first attempt to
291 visualize the deposition of iron particles (nano-scale) in the context of remediation with Fe⁰ was
292 recently published [67]. It is expected that the use of X-ray microtomography visualization (and
293 other appropriate techniques) will enable a better understanding of the effects of corrosion products
294 on the bed clogging and to interpret the evolution of the residual porosity.

295 An increase of the sustainability of the Fe⁰ bed is noticed (Tab. 5). More iron could be consumed at
296 the time t_{limit} . The extent of Fe⁰ depletion is increased by using admixtures. This result corroborates
297 the view that admixing Fe⁰ with non-expansive material is a tool to induce sustainability [14,24].
298 Accordingly, the repeatedly reported cost reduction (Fe⁰ costs) ([21] and ref. cited therein) should
299 be regarded as a positive side-effect. In other words, while using admixtures, material wastage [12]
300 is avoided and service life is increased. It seems that the Fe⁰ proportion in efficient real systems
301 should be lower than 50 % (1:1, v/v) used here [23,24]. In fact, the efficiently permeable reactive
302 barrier at Borden (Ontario, Canada) contained only 22 % Fe⁰ (w/w) [1]. On the other hand, while
303 testing Fe⁰ for viruses and bacteriophages removal from drinking, Shi et al. [68] found out that a
304 sand filter containing only 15 % Fe⁰ (w/w) was very efficient for microbe removal. The design of
305 Shi et al. [68] consisted in a column packed with sand (sand filter) containing a reactive Fe⁰/sand
306 layer (50:50, v/v). While the Fe⁰/sand ratio was the same as the one discussed here, this work and
307 related studies propose that parameters such as the characteristics of the column, the mass of Fe⁰,
308 the chemical reactivity of Fe⁰, the thickness of the Fe⁰/sand layer, the proportion of Fe⁰, the relative

309 size of used particles (δ values), the porosity of the additives are routinely given to enable the
310 comparison of results.

311 **4 Conclusions**

312 The concept that dual Fe^0 /inert additive systems are more sustainable than pure Fe^0 systems for
313 water treatment is validated using pumice and sand as additives and Cu^{II} , Ni^{II} and Zn^{II} as model
314 contaminants. As expected the sand system was more efficient for contaminant removal and the
315 pumice system more permeable. The order of contaminant removal efficiency corresponds to the
316 selectivity sequence for iron oxides. This observation corroborates the view that chemical reduction
317 (if applicable) is of secondary important for the process of contaminant removal.

318 The presented work highlights the volumetric expansive nature of iron corrosion as the most
319 important clogging factor in water treatment. Filter clogging is demonstrated to be related to pore
320 blocking in the inlet zone. Therefore, reliable strategies have to be developed to design sustainable
321 Fe^0 filters under environmental conditions (water works). Systematic research at laboratory scale is
322 needed to understand the impact of various factors on the clogging process. These factors include:
323 the temperature, the nature of Fe^0 (chemical reactivity) and used additives (reactivity, porosity), the
324 shape and dimension of Fe^0 and additives, the relative dimensions of Fe^0 and additives (δ values)
325 and the quality of the inflowing aqueous solution (pH, O_2 level, HCO_3^- , humic substances,
326 contaminants). The possibility to use various Fe^0 materials of different reactivity in the treatment
327 chains should be carefully considered. For example, a readily reactive Fe^0 material (e.g. powdered)
328 can be used in the first column(s) as O_2 scavenger and substituted when clogging occurs. In such a
329 configuration, less reactive materials (e.g. granular) are used in subsequent columns for effective
330 water treatment.

331 The net output of such a systematic research will be the minimization of uncertainties on the long
332 term efficiency (sustainability) of Fe^0 -based filtration systems, including nano-scale Fe^0 . The lack
333 of systematic approach has already led to difficulties in finding research funding [69] after more

334 than 15 years intensive research. Moreover, there is currently a hindrance in the spreading of this
335 efficient technology in Europe [70]. At the term, a small number of avoidable failures could result
336 in dismissal of a proven efficient technology.

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- 508
- 509

509 **Table 1:** Variability of the operational conditions for column experiments as illustrated by the
 510 dimension of the column (H, D), the nature of contaminants (X), the nature of additives, the Fe⁰
 511 mass, and the relative dimension of particles (δ).

512

X	H (cm)	D (cm)	Additive	Fe⁰ (g)	d_{Fe}^(*) (mm)	d_{additive}^(*) (mm)	δ^(**) (-)	Ref.
TCE, PCE	50	3.8	Sand	n.a.	0.25	1.315	0.19	[1]
As	31	2.5	Sand	75	0.42	0.275	0.65	[25]
NO ₃ ⁻	30	5	Sand	1636	0.3	n.a.	(-)	[26]
Cr	10	2.5	Sand	n.a.	1.45	0.638	0.44	[27]
As	17.8	5.1	Sand	400	0.15	0.4	0.38	[28]
As	4	0.1	Sand	1.5	n.a.	0.5	(-)	[29]
Cu	45	5	Sand	525	0.7	0.8	0.88	[30]
TCE	40	1.59	Sand	80	1.355	0.118	0.09	[21]
As	n.a.	n.a.	Sand	n.a.	0.5	0.5	1.0	[31]
NO ₃ ⁻	20	2	Sand	90	0.1	0.55	0.19	[32]
Cu, Ni	50	5	Pumice	240	0.5	0.30	0.6	[33]
Cu, Ni, Zn	50	5	Sand	200	0.5	0.28	0.6	present
Cu, Ni, Zn	50	5	Pumice	200	0.5	0.30	0.6	present

513

514 ^(*) d_{Fe} and d_{additive} are the the mean grain size of Fe⁰ and the additive respectively.

515 ^(**) δ is the diameter ratio of the smaller particle size to the larger one (Fe⁰ or additive).

516

517

517 **Table 2:** Characteristics of used materials tested by Mercury Intrusion Porosity (MIP).

518

	Fe ⁰	Pumice	Sand
Specific weight ρ_s (g/cm ³)	7.78	1.92	2.60
Apparent specific weight ρ_{as} (g/cm ³)	7.78	1.14	2.60
Compactness C(-)	0.51	0.45	0.55
Inter particular porosity Φ_{inter} (%)	49.6	54.8	45.0
Intra particular porosity ϕ_{pp} (%)	-	41.0	-
Porosity Φ_0 (%)	49.6	73.3	45.0

519

520

520 **Table 3:** Main characteristics of the studied columns. “ $r_{z_{eff}}$ ” is the measured reactive zone. The
 521 estimated porosity is also given.

System	Media	Fe⁰ (vol %)	Fe⁰ (g)	Additive (g)	Duration (days)	$r_{z_{eff}}$ (cm)	Porosity* (%)
A	sand	0.0	0.0	1060	28	40.0	45.05
B	pumice	0.0	0.0	27	28	2.6	72.6
C	Fe ⁰	100.0	200	0.0	17**	2.6	49.6
D	Fe ⁰ + sand	50.0	200	76.4	15**	5.2	46.05
E	Fe ⁰ + pumice	50.0	200	27.0	28**	5.0	59.5

522 * in this values the internal porosity of the pumice is also included.

523 **-marked systems were stopped because of excessive permeability loss.

524

525

526

527

527 **Table 4:** Magnitude of contaminant removal in investigated systems.

System	m_{in} (mg)			E (%)			Es (mg/g)		
	Ni	Cu	Zn	Ni	Cu	Zn	Ni	Cu	Zn
A	685	685	927	57.3	99.8	65.7	n.a.		
B	685	685	927	57.2	51.5	52.1	n.a.		
C	367	367	497	94.7	99.9	99.8	1.74	1.83	2.48
D	367	367	497	99.3	99.8	99.9	1.82	1.83	2.48
E	612	612	828	93.3	99.9	99.6	2.86	3.06	4.12

528

529

530

530 **Table 5:** Modelled characteristics of Fe⁰-containing columns. The extent of Fe⁰ depletion (%) is

531 given by: $\% \text{consumedFe} = 100 \cdot \frac{V_0 - V_t}{V_0}$ where $(V_0 - V_t)$ is the consumed Fe⁰ volume with V_0 the

532 initial volume of Fe⁰ and V_t its residual Fe⁰ at time t.

533

System	$t_{\text{limit}}^{(*)}$ (days)	Fe ⁰ depletion (%)	Fe ⁰ _{residual} (g)	$\Phi/\Phi_0^{(**)}$ (%)	E _{s,eff} (mg/g) ^(***)		
					Ni	Cu	Zn
Fe ⁰	7.5	17.1	168.8	4.6	5.0	5.0	6.8
Fe ⁰ :sand	10.0	33.2	133.6	2.0	4.0	4.1	5.5
Fe ⁰ :pumice	16.0	41.4	117.2	1.4	4.3	4.4	6.0

534

535 ^(*) “ t_{limit} ” is the time which corresponds to a constant hydraulic conductivity.

536 ^(**) Φ/Φ_0 is the residual porosity. Φ_0 is the initial porosity of the column.

537 ^(***) E_{s,eff} is the specific removal.

538

539

540

540 **Figure captions**

541

542 **Figure 1:** Schematic diagram of the experimental design. Used materials were (i) Fe⁰ (0 or 200 g),
543 (ii) pumice (0 or 27 g), and (iii) quartz gravel (0 or 1060 g).

544

545 **Figure 2:** Time-dependant evolution of the pH value (a) and the iron concentration (b) of column
546 effluent. The lines are not fitting functions, they simply connect points to facilitate visualization.

547

548 **Figure 3:** Magnitude of Cu (a), Ni (b), and Zn (c) breakthrough from the columns containing Fe⁰.
549 The lines are not fitting functions, they simply connect points to facilitate visualization.

550

551 **Figure 4:** Time-dependant evolution of the hydraulic conductivity in the three systems containing
552 Fe⁰ and the reference system pumice: (a) experimental K/K₀ values; (b, c and d) relative
553 permeability K/K₀, experimental and modelled values. $\eta = 6.4$, model 1: $t_{\infty, \text{depletion}} = 50$ days, and
554 model 2: $t_{\infty, \text{depletion}} = 62.5$ days. For the three Fe⁰-systems, the value at time t_{limit} has been adjusted so
555 that the residual content of Fe⁰ is slightly superior to the Fe⁰ volume which is not consumed at
556 clogging.

557