

26 **1 Introduction**

27 Packed beds with metallic iron (Fe^0) are currently used as contaminant mitigating agent in
28 several contexts including groundwater remediation, wastewater treatment and drinking water
29 production [1-4]. Fe^0 -based materials are used in particular (i) as reducing agents in
30 permeable reactive walls [5-8], and (ii) as reagents to assist biofiltration in household filters
31 [3,9,10]. The fundamental process responsible for contaminant removal in both contexts is
32 necessarily the oxidative dissolution of Fe^0 (iron corrosion) which may be coupled with
33 contaminant reduction (reactive walls) or the subsequent precipitation of iron hydroxides
34 which may be coupled with contaminant adsorption and co-precipitation (household filters).
35 Adsorption, co-precipitation and chemical transformations (oxidation and/or reduction) are
36 not mutually exclusive [11-13]. It is obvious that in household filters and reactive walls, a
37 synergy between these three processes is responsible for expected and observed
38 decontamination. Moreover, these processes proceed in the inter-granular porosity of the
39 packed beds which are made up of Fe^0 (100 %) or a mixture of Fe^0 and an inert material (e.g.
40 gravel, pumice, sand) [2,14]. Because of the volumetric expansive nature of the process of
41 iron corrosion [15], the porosity of the filtrating systems certainly decreases with increasing
42 service life, possibly yielding complete permeability loss system (filter clogging) [16,17]. The
43 filling of the pore volume by corrosion products is necessarily coupled with improved size
44 exclusion capacity. Therefore, a fourth mechanism for decontamination in packed Fe^0 beds is
45 identified.

46 The very recent concept that adsorption, co-precipitation and size exclusion are the
47 fundamental mechanisms of aqueous decontamination in Fe^0 packed beds [13] is yet to be
48 discussed in the scientific literature. The two main objectives of this communication are (i) to
49 give some arguments supporting the new concept, and (ii) to enumerate some consequences
50 for the further development of the iron filtration technology. In this effort a particular

51 attention is paid to filter dimensioning or bed sizing. For the sake of clarity, the presentation
52 will start with the short history of Fe^0 for reactive walls and household filters.

53 **2 Metallic iron for reactive walls**

54 The Fe^0 reactive wall technology is one aspect of the materialization of the original idea of
55 McMurty and Elton [18] that a passive design “using natural groundwater flow and a
56 treatment media” can “capture or treat the contaminants without the need for regeneration or
57 replacement”. With the publication of this innovative concept in August 1985, an ongoing
58 effort for efficient reactive materials for permeable reactive barriers started. In 1990, Gillham
59 and his colleagues fortuitously found that corroding Fe^0 (reductively) eliminated aqueous
60 trichloroethylene [19]. This discovery was the starting point of remediation with elemental
61 metals. Elemental metals (e.g. Al^0 , Fe^0 , Zn^0 and bimetallics) are now recognized as competent
62 alternatives for remediation of groundwater that is contaminated with reducible substances
63 [8,20].

64 Currently, however, Fe^0 has exceeded all expectations because non-reducible substances have
65 been quantitatively removed as well. For example, aqueous Zn^{II} which is thermodynamically
66 non-reducible by Fe^0 has been efficiently removed [21]. The results of Morrison et al. [21]
67 attested the synergic effects of removal mechanisms as the investigated systems also
68 contained Mo^{VI} and U^{VI} . Mo^{VI} and U^{VI} could be reduced to less soluble species. Furthermore,
69 Mo^{VI} known for its poor adsorptive capability onto iron oxides at $\text{pH} > 5$ [22,23] was
70 quantitatively removed, suggesting that improved size exclusion might had been effective.

71 The concept that contaminants are fundamentally removed by adsorption and co-precipitation
72 is consistent with many experimental observations which remained non-elucidated by the
73 reductive transformation concept [11,12]. Although researchers are continuing to maintain the
74 validity of the latter concept [24-26], the new concept was validated [27,28] and has been
75 independently verified [29,30]. As a matter of course the concept of adsorption/co-
76 precipitation (and size exclusion for packed bed) should have been challenged by researchers

77 working on remediation in $\text{Fe}^0/\text{H}_2\text{O}$ systems. The motivation of using Fe^0 at household level
78 corroborates the validity of the adsorption/co-precipitation/size exclusion concept.

79 **3 Metallic iron for household filters**

80 While using slow sand filtration for water treatment in rural Bangladesh, it was observed that
81 the filter efficiency for arsenic removal depends on the iron content of natural waters. Arsenic
82 was readily removed from Fe-rich natural waters. Accordingly, Fe^0 is used “to provide a
83 constant input of iron (soluble or surface precipitate) for groundwater low in soluble iron”
84 [32]. The very efficient resulting filter for As removal was the 3-Kolsi filter [10,33]. A typical
85 3-Kolsi filter contained a layer of about 3 kg Fe^0 (100 % Fe^0). However, the 3-Kolsi filter was
86 not sustainable as it clogged after some 8 weeks of operation [3,34].

87 The remarkable efficiency of 3-Kolsi filters has prompted researchers to further develop the
88 system for improved sustainability [9,10,31,34-37]. The best product is the SONO arsenic
89 filter in which the 100 % Fe^0 layer is replaced by a proprietary porous Fe^0 -based material
90 (termed as Composite Iron Material - CIM) [32,33]. The two most important features of CIM
91 are: (i) its porosity and (ii) its low content of Fe^0 . In consequence, two opposite effects may
92 be observed: (i) the porous structure of the CIM induces a larger reactive surface compared to
93 non-porous Fe^0 particle (or compact Fe^0); the internal porosity could be regarded as magazine
94 for in-situ generated iron corrosion products and (ii) less initial Fe^0 is used compared to
95 compact Fe^0 particle. The former effect (larger reactive surface) is well-documented as tool to
96 improve Fe^0 efficiency and is the rationale for using nano-scale Fe^0 for water treatment [38].
97 The latter effect (less initial Fe^0) could not improve Fe^0 efficiency in term of Fe^0 reactivity but
98 is known as tool to delay or avoid porosity loss [39-41]. of the filter system, but not the
99 second. These observations suggest that the 100 % Fe^0 layer in the 3-Kolsi filter was the
100 major reason for its too short service life. Leupin and Hug [35] have considerably reduced the
101 proportion of Fe^0 (1.5 g Fe^0 for 60 g sand). More recently, Gottinger [42] demonstrated in a

102 pilot study that a volumetric mixture Fe^0 :sand of 30:70 was very efficient for water treatment
103 at a small community level.

104 It is important to notice that household Fe^0 filters primarily treat water of unknown
105 composition. Design efforts are focused on keeping filter permeability. Available filters were
106 designed for As removal but SONO filters have efficiently removed several other chemicals
107 and pathogens [32,43,44]. It is obvious that Fe^0 -based filters regarded as “ Fe^0 assisted sand
108 filtration” are not designed to chemically reduce any contaminant. Even arsenics for which
109 the majority of household filters were designed is removed by adsorption, co-precipitation
110 and size exclusion, although As^{V} reduction to As^{III} and As^0 is thermodynamically favorable
111 ([3,45] and references therein).

112 A typical SONO filter contains 5 to 10 kg of porous CIM (CIM: 92 - 94 % Fe, 4 - 5 % C, 1 - 2
113 % SiO_2 , 1 - 2 % Mn, 1 - 2 % S,P) and may function for up to 11 years while filtering waters
114 containing up to 1000 $\mu\text{g As/L}$. It is important to notice that only a fraction of the 92 - 94 %
115 Fe in SONO filters is in metallic form (Fe^0) and could undergo volumetric expansion.
116 Therefore, learning from SONO filters to design efficient Fe^0 beds consists in reducing the
117 proportion of Fe^0 and create place for in-situ generated iron corrosion products. Prior to
118 discuss an efficient designing tool, an overview of current design options to limit the impact
119 of fouling in Fe^0 PRB will be given.

120 **4 Current design approach to limit Fe^0 PRB clogging**

121 Fe^0 PRBs are currently believed to create redox conditions for contaminant degradation or
122 immobilization [2]. Accordingly, the precipitation of iron corrosion products and other
123 secondary minerals is regarded as perturbing side effect yielding reactivity and porosity loss
124 [2,14,16,17]. Accordingly, the design of a PRB requires profound knowledge of local water
125 flow velocity (residence time), aquifer porosity, influent contaminant concentration.
126 Additionally, the contaminant degradation rate by used Fe^0 is usually estimated in laboratory
127 and pilot studies and used to size the PRB. Sizing aspects include the amount of Fe^0 to be

128 used and the thickness of the bed (filter or wall). The first problem with this approach is that
129 used Fe⁰ media can not be each other compared in reactivity as there is no standard procedure
130 to this end [46].

131 Recently, Li and Benson [2] identified and discussed five relevant strategies to limit the
132 clogging of Fe⁰ PRBs: (i) pea gravel equalization zones up gradient and down gradient of the
133 reactive zone to equalize flows (strategy 1), (ii) placement of a sacrificial pre-treatment zone
134 upstream of the reactive medium (strategy 2), (iii) pH adjustment (strategy 3), (iv) use of
135 larger Fe⁰ particles (strategy 4), and (v) periodic mixing of the Fe⁰ to break up and redistribute
136 secondary minerals (strategy 5).

137 In the light of the concept that contaminants are basically removed by adsorption, co-
138 precipitation and size exclusion, the following comments can be made on the five strategies.
139 Strategy 1 necessarily has a double function as quantitative contaminant removal may occur
140 in the equalization zones. The same remark is valid for strategy 2 as this study shows that
141 reactive zones with 100 % Fe⁰ are not sustainable. Strategy 3 is recommended because iron
142 corrosion is sustained by FeS₂ dissolution (or H⁺ production). Accordingly, FeS₂ should be
143 regarded as useful reactive additive (Fe⁰/FeS₂ system or Fe⁰/FeS₂/sand system). Hereby, care
144 should be taken that the added proportion of FeS₂ don't induce a pH shift below a value of
145 5.5. In fact, if the final pH < 5.5 the Fe solubility is increased and the effluent may exhibit too
146 high Fe concentration. On the other hand, if dissolve Fe is transported away from the reactive
147 zone, the bed porosity will increase and the filtration efficiency will decrease. Another
148 positively tested reactive additive is MnO₂ [29,47,48]. MnO₂ reductive dissolution is driven
149 by Fe^{II} from Fe⁰ oxidation, sustaining Fe⁰ dissolution is beneficial for the decontamination
150 process. Strategy 4 will be effective only at certain sites depending on the extent of
151 contamination. In fact, larger size Fe⁰ means larger pore space and poorer size exclusion.
152 Finally, Strategy 5 can be rendered superfluous by a proper bed design.

153 The approach based on the concept that contaminants are removed by adsorption, co-
154 precipitation and size exclusion has the advantage that only iron corrosion with site-specific
155 water or relevant model water has to be characterized for proper barrier design. Accordingly,
156 an aggressive groundwater will rapidly corrode iron, rendering a thin wall satisfactorily. For
157 less aggressive waters a thicker wall is necessary to enable completed contaminant removal
158 by multi-filtration (see discussion section). The same systematic can be applied to Fe⁰ media
159 of various reactivity. The less reactive a material in a groundwater, the thicker the reactive
160 barrier. Therefore, the selection of the most appropriate Fe⁰ material at each site is a key issue
161 for wall or generally bed efficiency. The next section is focused on better designing Fe⁰ beds.

162 **5 Designing Fe⁰ beds**

163 The presentation above suggests that Fe⁰ bed design must be based on the available pore
164 volume for volumetric expansion of corroding iron. Accordingly, for a given bed size
165 replacing a portion of reactive iron by an inert material is the first tool to extend filter service
166 life. The very first additive material in this regard is a non-porous material as quartz (0 %
167 porosity). The next step could consist in partly or totally replacing quartz by porous materials
168 like sandstone (up to 40 % porosity) or pumice (up to 90 % porosity). In each case a critical
169 Fe⁰:additive ratio must exist for which bed porosity is lost upon Fe⁰ depletion as illustrated
170 below.

171 **5.1 Sustaining Fe⁰ bed reactivity by addition of inert materials: Bed design**

172 A random packed Fe⁰ bed of identical spheres is considered. The initial bed porosity Φ_0 has a
173 fundamental value of 36 % [49]. In other words, regardless from the actual dimension of the
174 bed, 64 % of the bed volume V is filled by dense Fe⁰ and 36 % is available as inter-granular
175 pore space for corrosion products. It can be noticed that the compactness C of the granular
176 medium is $C=1-\Phi_0=V_{\text{initial Fe}} / V=0.64$ where $V_{\text{initial Fe}}$ is the initial volume of iron. If a
177 volumetric fraction of Fe⁰ is replaced by non-porous quartz (with the same particle diameter),
178 36 % of the bed volume is still available for corrosion products but more Fe⁰ will corrode

179 before the bed porosity decreases to zero (Fig. 1). Calculations could enable the identification
180 of critical Fe⁰:additive ratios. Two hypothetical examples will be used here for illustration: (i)
181 a rectangular reactive wall, and (ii) a cylindrical household filter.

182 The dimensions of the demonstration reactive wall in Borden (Ontario, Canada) are used for
183 the hypothetical reactive wall [5]. The dimensions of the wall were 5.5 x 1.6 x 2.2 m (l x w x
184 h), giving a volume $V = 19.36 \text{ m}^3$. For the hypothetical cylindrical household filter the
185 dimensions of field columns used by Westerhoff and James [49] are adopted. The columns
186 had a total capacity or volume $V = 4.022 \cdot 10^{-3} \text{ m}^3$ (4.022 L): diameter 7.5 cm and height 91
187 cm.

188 The filling of the bed porosity by iron corrosion products can be estimated from a simplified
189 modeling (Fig. 1) based on the following assumptions:

190 (i) uniform corrosion: the diameter reduction of the particle is the same for all the Fe⁰
191 particles,

192 (ii) iron corrosion products are fluid enough to progressively fill available pore space.

193 Assuming that the coefficient of volumetric expansion (η) of the iron corrosion products is:

$$194 \quad \eta = V_{\text{oxides}}/V_{\text{Fe}} \quad (1)$$

195 where V_{oxides} is the volume of the iron corrosion products and V_{Fe} the volume of parent Fe⁰.

196 The surplus volume of the iron corrosion products contributing to porosity loss is V'_{oxides} . Per
197 definition V'_{oxides} is the difference between the volume V_{oxides} of iron corrosion products and
198 the volume V_{Fe} of parent Fe⁰. V'_{oxides} is given by Eq. 2:

$$199 \quad V'_{\text{oxides}} = (\eta - 1) * V_{\text{Fe}} \quad (2)$$

200 Assuming that the bed is clogged when the volume V'_{oxides} is equal to the initial inter granular
201 voids ($\Phi_0 \cdot V$), the volume $V_{\text{Fe, clogging}}$ of the consumed iron leading to clogging of the bed is
202 then estimated by:

$$203 \quad V_{\text{Fe, clogging}} = \frac{\Phi_0 \cdot V}{\eta - 1} \quad (3)$$

204 In this case (Eq.3), the volume $V_{\text{Fe, clogging}}$ of the consumed iron is inferior to the initial
205 volume of dense Fe^0 . It means that clogging appears before depletion of Fe. It can be noticed
206 that, in some cases, the initial volume of iron may be too low so that there is no clogging and
207 the bed porosity is not completely filled by iron corrosion products.

208 The residual porosity Φ_r defined by $\Phi_r = V_{\text{residual voids}} / V$ is evaluated by Eq. 4:

$$209 \quad \Phi_r = \Phi_0 - (\eta - 1) \cdot \frac{V_{\text{consumedFe}}}{V} \quad (4)$$

210 where $V_{\text{consumedFe}}$ is the volume of Fe which is consumed. When the clogging appears before
211 depletion of Fe^0 , the volume $V_{\text{consumedFe}}$ is given by the equation 3 and the residual porosity is
212 equal to $\Phi_r=0$. When there is no clogging, the volume $V_{\text{consumedFe}}$ is equal to the initial volume
213 of Fe and there is residual porosity ($\Phi_r \neq 0$).

214 These calculations allow the evaluation of the efficiency of the bed (reactive wall or filter)
215 related to the possible clogging. Two cases are discussed in the following.

216 **5.2 Case of a 100 % Fe^0 bed**

217 Considering that the density of Fe^0 is $7,800 \text{ kg/m}^3$, the 12.4 m^3 (64 % of the total volume)
218 available in the hypothetical reactive wall (Tab. 1) can be filled by 96,645 kg of Fe^0 . The
219 calculations in Tab. 2 demonstrated that from this Fe^0 amount only a maximum of 50,336 kg
220 can be oxidized to yield porosity loss (no residual porosity, $\Phi_r=0$). The weight proportion of
221 consumed Fe^0 ranges between 10.4 % and 52.1 % when the main corrosion products are
222 $\text{Fe}(\text{OH})_3 \cdot 3\text{H}_2\text{O}$ (ferrihyrite) or Fe_2O_3 (hematite) respectively, showing that 100 % Fe^0 reactive
223 walls are pure material wastage. The calculations for the hypothetical household filter
224 demonstrated that only 2.1 to 10.5 kg of Fe^0 will be consumed corresponding to the same
225 weight percent like for the hypothetical reactive wall.

226 Ideally, when Fe^0 is mixed with quartz, a bed containing more than 52.1 wt-% Fe^0 of the mass
227 of Fe^0 necessary to have a 100 % Fe^0 bed should not be constructed because bed clogging will
228 happen and excess Fe^0 will not react (material wastage). The actual Fe^0 proportion will

229 depend on its intrinsic reactivity and the kinetics of iron oxidative dissolution. Kinetics
230 aspects are not considered in this study.

231 **5.3 Case of a volumetric Fe⁰:quartz ratio of 50:50**

232 The calculations above suggests that only about 10.4 to 52.1 wt-% Fe⁰ is necessary to fill the
233 pore space of a 100 % Fe⁰ filter regardless from the bed dimensions. In this section, the
234 calculations are made for a volumetric Fe⁰:quartz ratio of 50:50. To calculate the
235 corresponding weight ratio, one should use the particle size and the densities. However,
236 because the same beds (wall and filter) are used, the bed volume occupied by 50 vol-% is
237 necessarily one half of the value used in the pure Fe⁰ bed: (i) 6.20 m³ or 48,322 kg for the
238 wall and (ii) 1.3*10⁻³ m³ (1.3 L) or 10.4 kg for the filter. It is evident that the Fe⁰ masses
239 consumed to yield bed clogging are the same as in the 100 % Fe⁰ case. The percent
240 consumption is then higher (more iron is consumed to obtain the same volume of iron
241 corrosion products at Fe⁰ depletion, Fig. 1 and varies from 21 % for Fe(OH)₃.3H₂O to 100 %
242 for Fe₂O₃ and Fe₃O₄.

243 The bed containing 50 vol-% Fe⁰ is necessarily clogged at Fe⁰ depletion; no residual porosity
244 ($\Phi_r=0$). However, an ideal treatment system should keep a certain residual porosity. This is
245 particularly important for subsurface reactive barriers. To warrant a residual porosity ($\Phi_r \neq 0$)
246 while using a constant Fe⁰ amount in the bed, it appears that thicker beds have to be
247 considered. For example the amount of additive material can be increased such that the
248 resulting volumetric proportion of Fe⁰ is 35 %. Another tool to sustain Fe⁰ reactivity is to use
249 porous additive instead of non-porous quartz. In this way, the total volume for the storage of
250 in-situ generated iron corrosion products is increased and the residual bed porosity at Fe⁰
251 depletion is warranted as will be illustrated in the next section.

252 **5.4 Lengthening Fe⁰ bed service life by porous additives**

253 When quartz particles from section 5.3 are replaced by V_{PP} of porous particles (with V_{PP} = V -
254 V_{initial Fe}), the available porosity Φ_0' for iron corrosion products is increased according to:

255
$$\Phi_0' = \Phi_0 + \varphi_{pp} \cdot f_{pp} \quad (5)$$

256 where φ_{pp} (-) is the critical porosity of the porous particles;

257 f_{pp} (-) is the porous particle volume fraction (here $f_{pp} = V_{pp}/V$).

258 The volume V_{Fe} of the consumed iron leading to clogging of the bed (Eq. 3) or the residual
259 porosity Φ_r (Eq. 4) can be obtained by replacing Φ_0 by Φ_0' . The calculations in Tab. 3 show
260 that it is possible to increase the efficiency of the filtration system. More iron may be
261 consumed and transformed into iron corrosion products before clogging. In two cases (Fe_2O_3
262 and Fe_3O_4), a residual bed porosity is available at Fe depletion.

263 Figure 2 shows that replacing quartz by sandstone or more porous (or less dense) materials
264 could further extend Fe^0 bed service life. This conclusion is justified by the fact that heavier
265 materials are less porous. However, the most important feature from Fig. 2 is that weight-
266 based and volumetric ratios are not linearly dependent. Therefore, the description of any
267 experimental design should comprise data on Fe^0 and additives (form, density, porosity, size)
268 and filter dimensions together with the volumetric proportion of Fe^0 . This procedure will
269 enable or ease comparability of published results.

270 **5.5 Discussion**

271 The calculations above have shown that in a 100 % Fe^0 bed, system clogging will occur when
272 only about 52 wt-% of used Fe^0 is consumed. In a 50 % Fe^0 bed material depletion (100 %
273 consumption) is only possible if the corrosion products are Fe_3O_4 and Fe_2O_3 (no residual
274 porosity). By replacing quartz by sandstone, a residual porosity Φ_r about 12 % is obtained
275 when the corrosion products are Fe_3O_4 and Fe_2O_3 . But even in these cases, crystalline Fe_3O_4
276 and Fe_2O_3 are the final stages of transformations which go through several more volumetric
277 amorphous stages (e.g. $Fe(OH)_2$, $FeOOH$). Accordingly, a volumetric ratio 50:50 should be
278 regarded as the highest proportion of Fe^0 for long-term efficiency of Fe^0 beds. In the literature
279 however, a 50:50 weight ratio is usually used based on a pragmatic approach [50]. The

280 volumetric 50:50 ratio for the Fe^0 :quartz mixture (quartz: 2.6 kg/m^3) corresponds to a
281 Fe^0 :quartz weight ratio of 75:25. The suitability of the volumetric ratio in this context arises
282 from the fact that the expansive nature of iron corrosion is to be considered. Finally, a
283 consideration of the conditions used by O'Hannesin and Gillham [5] and Westerhoff and
284 James [50] is made.

285 O'Hannesin and Gillham [5] used only 22 wt-% Fe^0 in the reactive wall in Borden (Ontario
286 Canada). This proportion corresponds to less than 10 vol-% Fe^0 showing that the
287 demonstration wall at Borden is highly permeable. Accordingly, system clogging due to
288 expansive iron corrosion is not expected because the available pore space is by far larger than
289 the volume of iron corrosion products at Fe^0 depletion. As discussed in section 4, most Fe^0
290 PRBs contain a zone with 100 % Fe^0 . In some cases "equalization zones" and a "sacrificial
291 pre-treatment zone" exist in which Fe^0 is mixed with gravel or sand. In recent barriers mixing
292 Fe^0 and sand is considered as a tool to save expense for Fe^0 media [51]. However, the proper
293 consideration of the expansive nature of Fe^0 corrosion shows that mixing Fe^0 and inert
294 material is a prerequisite for long service life.

295 Westerhoff and James [50] could evidence the difficulty of performing long-term experiment
296 with 100 % Fe^0 beds. A weight-base 50:50 Fe^0 :sand bed could perform accurately for several
297 months (12 months). Similarly, household 100 % Fe^0 filters were abandoned because of rapid
298 clogging [10,32]. The calculations above rationalize the current renaissance of Fe^0 filter
299 technology for household filters [52] and its use for small scale water facilities [42,53]. Fe^0
300 filter technology is regarded as a flexible and affordable technology, which could enable the
301 achievement of the Millennium Development Goals (MDGs) for water. This simple technology
302 could even enable to achieve universal access to safe drinking water within some few years
303 [52].

304 **6 General discussion**

305 **6.1 Fe^0 bed as adsorptive size-exclusion system**

306 The consideration of Fe⁰ beds as adsorptive size-exclusion systems arises from the strong
307 adsorptive properties of in-situ generated iron corrosion products [54]. Iron is progressively
308 corroded (uniform corrosion) in the whole bed. Contaminants are removed by adsorption, co-
309 precipitation and size exclusion within the whole bed. Removed contaminants could be
310 further chemically transformed (oxidized or reduced). A contaminant that is not removed in
311 the entrance zone could be removed deeper in the Fe⁰ bed (deep-bed filtration). This
312 behaviour is illustrated the best by simple experiments by Leupin and Hug [34]. These
313 authors performed an As removal experiment in a series of four filters. Each filter contained
314 1.5 g iron and 60 g sand. The system with a total of 6 g iron could efficiently filtered 36 L of
315 an aqueous solution containing 500 mg As/L. A close consideration of the filtration efficacy
316 pro filtration event showed that less than 20 % (100 mg As/L) of the initial arsenic was
317 removed during the first filtration; a much larger fraction (≥ 200 mg As/L) was removed
318 during the second filtration, arsenic removal continued during the third and fourth filtration. It
319 is important to note that Fe⁰ was not depleted in the experiments and the filters were not
320 clogged. Accordingly, further As removal occurred even though As breakthrough ([As] > 50
321 $\mu\text{g/L}$) was observed. The Fe⁰ weight percent of 2.4 was necessarily too low for efficient
322 filtration in a single event, but has the advantage to avoid the clogging of the filter. However,
323 this experiment demonstrated the deep-bed filtration nature of individual Fe⁰ beds which
324 could equally be demonstrated with four sample ports on a single bed.

325 For the further illustration of deep-bed filtration nature of Fe⁰ beds, Fig. 3 compares the
326 breakthrough of contaminants in a granular activated carbon (GAC) bed and a Fe⁰ bed. To be
327 treated, water is applied directly to the upper end and allow to flow through the packing bed
328 by gravity.

329 GAC is inert in water and the adsorption capacity is consumed only by contaminants which
330 displace H₂O from adsorption sites. Accordingly, the region where contaminant adsorption
331 takes place is called the mass-transfer zone (or adsorption front). The region above the

332 adsorption front is the saturated zone and the region below is the virgin zone. As a function of
333 time, the saturated zone moves through the bed and approaches the end [54]. The adsorption
334 bed is exhausted when no more satisfactorily decontamination is achieved.

335 On the contrary, in a Fe^0 bed, the whole bed is available as sorption, co-precipitation and size
336 exclusion system. A sort of “adsorption front” may exist because of increased oxidizing
337 agent’s levels in the inflowing solution. However in the whole bed H_2O corrodes Fe^0
338 producing corrosion products for efficiency contaminant removal. Contaminant removal may
339 thus occur deeper in the Fe^0 bed from the initial stage of bed service on.

340 **6.2 Significance for system design**

341 The scientific community has long been searching for common underlying mechanisms for
342 the process of contaminant removal in $\text{Fe}^0/\text{H}_2\text{O}$ systems that provide a confidence for design
343 that is non-site-specific [57,58]. This was the idea behind introducing specific reaction rate
344 constant (k_{SA}). k_{SA} values are regarded as a more general reactivity descriptor of contaminants
345 with Fe^0 . They are also believed to allow intersystem comparisons [56]. However, there are
346 two major problems with the k_{SA} concept: (i) it is contaminant specific, and (ii) it is based on
347 the concept of reductive transformation which is definitively not determinant for the process
348 of the removal of several contaminants.

349 While previous efforts were directed at achieving a significant body of removal rate for
350 individual contaminants in order to enable non-site specific bed design, the present study
351 suggests that site-specificity will govern material selection. For example, if contaminated
352 water is carbonate-rich, it could be advantageous to use a relative low reactive material which
353 corrodibility will be sustained by carbonates. Accordingly, if available Fe^0 is classified for
354 specific conditions, treatability studies may only be required to fine-tune design criteria for
355 the optimal Fe^0 bed performance.

356 **7 Concluding remarks**

357 This study clearly delineates the important role of volumetric expansion of corroding iron for
358 the process of contaminant removal in Fe^0 beds and the sustainability of Fe^0 beds.
359 Sustainability is primarily warrant by admixing Fe^0 with non reactive additives to avoid or
360 delay porosity loss. The characterization of Fe^0 beds by the volumetric Fe^0 :additive ratios and
361 the bed sizes provide a clear starting point for the design of future laboratory, pilot, and field-
362 scale studies aiming at characterizing remediation Fe^0 beds. This certainly has economic
363 implications for Fe^0 bed design as the use of too high Fe^0 amount (e.g. > 60 vol-%) has to be
364 avoided. Most importantly results will be more comparable, accelerating progress in
365 technology development.

366 The most important result from the calculations of this study is that, for a given Fe^0 amount,
367 necessary for efficient decontamination at a specific contaminated site, building a thicker
368 barrier in which iron represents a volumetric proportion of 30 to 45 % is more advantageous
369 than a thin barrier containing more than 60 vol-% iron. A further useful tool to extend Fe^0 bed
370 service live is to use porous additives which allow avoiding/delaying bed clogging.

371 The installation of thicker reactive walls in the underground is certainly coupled with elevated
372 investment costs. However, thickening the barrier is essential for barrier sustainability (deep-
373 bed filtration). For household filters and Fe^0 beds in water treatment plants [42,53] the
374 achievement of multi-filtration is an easier task as for instance, several beds could let to
375 operate in series.

376 Finally, it should be highlighted that the very first reactive wall constructed at Borden
377 (Ontario, Canada) for the demonstration of the feasibility of the new technology contained
378 less than 10 vol-% (Fe^0) and could never been clogged because the porosity of the system
379 could not be filled by expansive iron corrosion products. In other words because of
380 insufficient system analysis, the Fe^0 reactive wall technology was demonstrated on a very
381 permeable system but operating walls are necessarily less permeable. Moreover, mixing Fe^0
382 and sand was considered as a tool to reduced Fe^0 costs [51,52]. It is now demonstrated, that

383 mixing Fe⁰ with inert additives is even the prerequisite for sustainability. It is hoped that the
384 huge literature on deep-bed filtration [59,60] will now be used for the further development of
385 iron wall technology.

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389 Chemical Engineering Journal.

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540

541

541 **Table 1:** Mass of material necessary to completely fill the hypothetical treatment units with
 542 100 % metallic iron. The fundamental porosity of $\Phi_0 = 36\%$ is assumed and the
 543 value of $7,800 \text{ kg/m}^3$ is taken for the specific weight of Fe^0 .

Unit	V_{unit} (m ³)	V_{Fe} (m ³)	V_{pores} (m ³)	m_{Fe} (kg)
Filter	0.004	0.0026	0.0014	20.08
Wall	19.4	12.4	6.97	96,645

544

545

546

546 **Table 2:** Mass (m_{wall} or m_{filter} in kg) of iron and weight proportion of consumed iron (P in %,
547 same value for the wall or the filter) leading to porosity loss in the hypothetical
548 field reactive wall and household filter as function of the nature of corrosion
549 products. Φ_r is the residual porosity (in this case $\Phi_r = 0$ and iron is not completely
550 consumed, $P < 100\%$). $V_{\text{oxid}}/V_{\text{Fe}}$ values are expansive coefficients from Ref. [15].

551

Oxid	$V_{\text{oxid}}/V_{\text{Fe}}$	m_{wall}	m_{filter}	P	Φ_r
		(kg)	(kg)	(%)	(%)
1/2 Fe ₂ O ₃	2.08	50,336	10.45	52.1	0
1/3 Fe ₃ O ₄	2.12	48,538	10.08	50.2	0
γ -FeOOH	3.03	26,779	5.56	27.7	0
β -FeOOH	3.48	21,920	4.55	22.7	0
Fe(OH) ₂	3.75	19,768	4.11	20.5	0
α -FeOOH	3.91	18,681	3.88	19.3	0
Fe(OH) ₃	4.2	16,988	3.53	17.6	0
Fe(OH) ₃ .3H ₂ O	6.4	10,067	2.09	10.4	0

552

553

553 **Table 3:** Weight proportion P of consumed iron leading to porosity loss (Eq. 3) or residual
 554 porosity Φ_r (Eq. 4) as function of the nature of corrosion products for
 555 Fe⁰:sandstone with a volumetric ratio 50:50. $V_{\text{oxid}}/V_{\text{Fe}}$ values are expansive
 556 coefficient from Ref. [15]. The critical porosity of sandstone is 40% and its
 557 specific weight is 2.0 kg/m³. The results are the same for the reactive wall and the
 558 household filter.

559

Oxid	$V_{\text{oxid}}/V_{\text{Fe}}$	P	Φ_r
		(%)	(%)
1/2 Fe ₂ O ₃	2.08	100	14.2
1/3 Fe ₃ O ₄	2.12	100	12.9
γ -FeOOH	3.03	75.1	0
β -FeOOH	3.48	61.5	0
Fe(OH) ₂	3.75	55.5	0
α -FeOOH	3.91	52.4	0
Fe(OH) ₃	4.2	47.7	0
Fe(OH) ₃ .3H ₂ O	6.4	28.2	0

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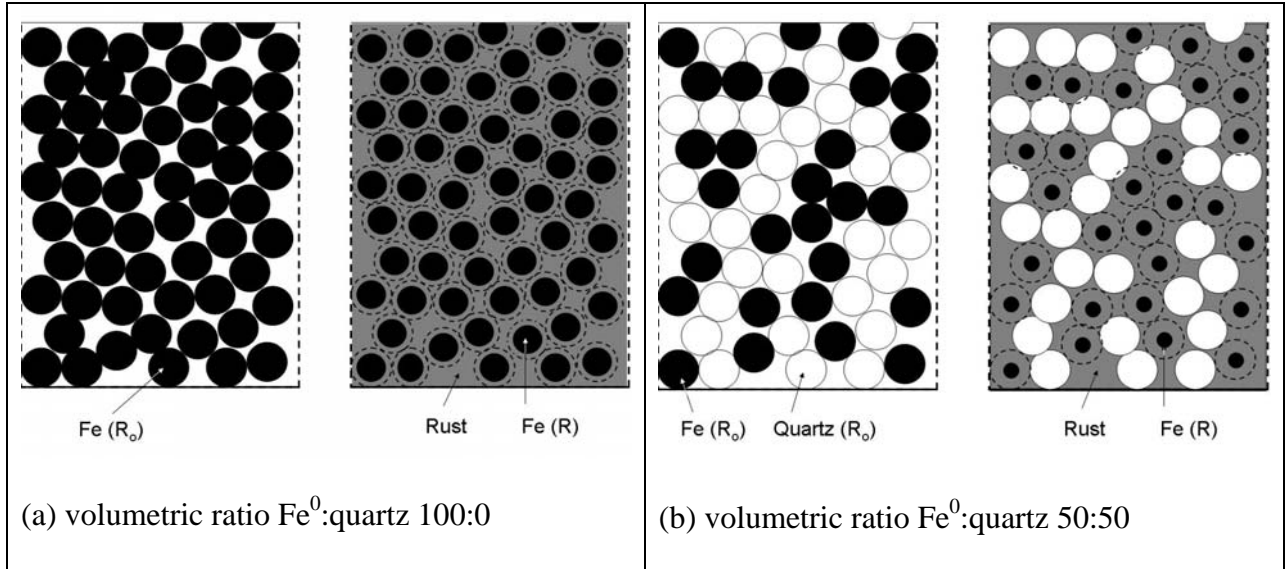
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562 **Figure 1**

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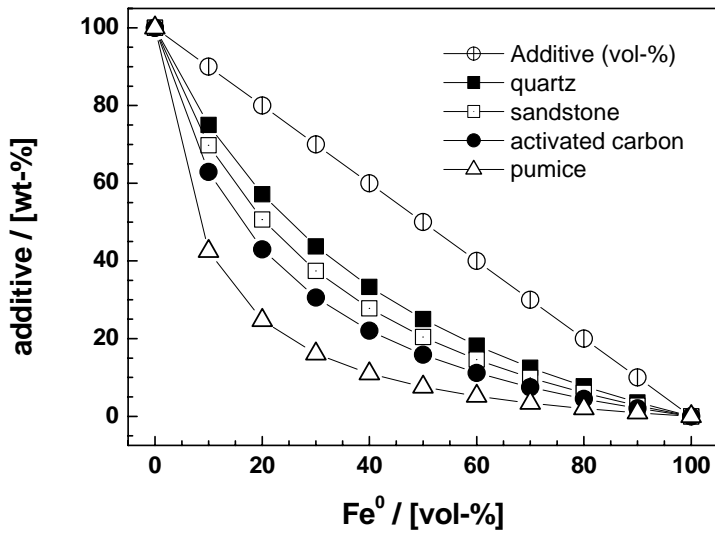
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567 **Figure 2**

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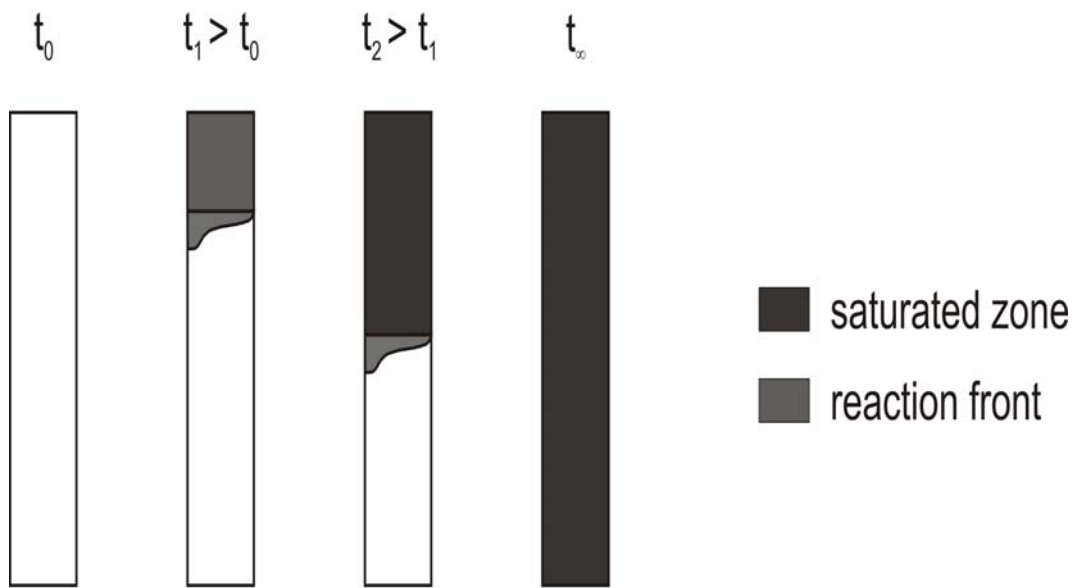
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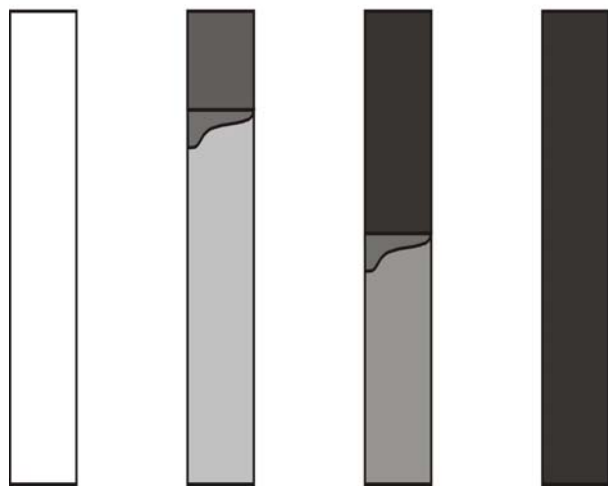
573 **Figure 3**

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576 **Figure captions**

577

578 **Figure 1:** Schematic illustration of the impact of mixing Fe^0 and quartz for the long-term
579 reactivity of Fe^0 beds (clogging). When Fe^0 is mixed with quartz more iron corrodes and the
580 initial porosity is progressively filled with porous iron oxides for water multi-filtration.

581

582 **Figure 2:** Variation of the weight percent of additive materials as function of the Fe^0
583 volumetric ratio. Due to the differences in density, there is no linear dependence. The depicted
584 variation of the wt-ratio depends on the material density. Used density values are: Fe^0 : 7.80
585 g/cm^3 , quartz: 2.65 g/cm^3 , sandstone: 2.00 g/cm^3 , activated carbon: 1.47 g/cm^3 , and pumice
586 0.64 g/cm^3 .

587

588 **Figure 3:** Comparison of the evolution of contaminant loading in granular activated carbon
589 (GAC - up) and Fe^0 (down) filters. The evolution of the GAC filters is virgin - preloaded
590 (reaction front) and saturated carbon. For the Fe^0 filters a reaction front may exist due to
591 increased O_2 in the influent but iron corrosion by H_2O (or H^+) occurs uniformly in the whole
592 column. The light grey shadow indicates progressive Fe^0 corrosion by water.

593