

# Investigating the Processes of Contaminant Removal in Fe<sup>0</sup>/H<sub>2</sub>O Systems

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## Abstract

The instability of the premise of direct quantitative contaminant reduction by elemental iron (Fe<sup>0</sup>) materials in Fe<sup>0</sup>/H<sub>2</sub>O systems is pointed out. Recalled basic knowledge on aqueous iron corrosion shows that Fe<sup>0</sup> surface is not available for decontamination in nature. A comparison of the reactivity of Fe<sup>0</sup> and Zn<sup>0</sup> shows that the effectiveness of Fe<sup>0</sup> materials for environmental remediation is due to the formation of a non-adhesive, porous oxide scale on Fe<sup>0</sup>. Contaminants are enmeshed within the scale and possibly reduced by primary Fe<sup>II</sup> and H<sub>2</sub>. An evaluation of current experimental conditions shows that well-mixed batch systems have disturbed the process of scale formation. Therefore, the majority of published works has operatively created conditions for contaminant reduction that are not likely to occur in nature. Since working under such unrealistic conditions has mediated the above mentioned premise, interactions in Fe<sup>0</sup>/H<sub>2</sub>O systems yielding contaminant removal should be revisited.

**Keywords:** Adsorption, Decontamination, Reduction, Remediation, Zerovalent iron.

## 27 **1 Introduction**

28 The strong oxidation state dependent toxicity of several pollutants has prompted the  
29 development of remediation strategies that stimulate redox reactions in wastewaters,  
30 contaminated soils, sediments, and groundwater [1-13]. Thereby, hazardous species are  
31 transformed to less toxic or less mobile species through a redox reaction. For example,  
32 chromium(VI) reduction to chromium(III) substantially decreases this metal's solubility,  
33 mobility, and toxicity [12,14]. The same principle governs the expected reduction of  
34 uranium(VI) to uranium(IV) [15-17]. Tested geochemical approaches included injection of  
35 reactive solutions [18,19], permeable reactive walls of elemental iron materials [4,20,21] or  
36 other reactive minerals such as  $\text{FeS}_2$  and  $\text{FeCO}_3$  [22-24], and injection of  $\text{H}_2\text{S}$  [25].  
37 Biogeochemical strategies rely on supplying organic carbon (OC) to stimulate direct  
38 microbial transformation of pollutants and indirectly microbially mediated reactions [26,27]:

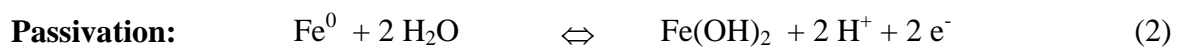
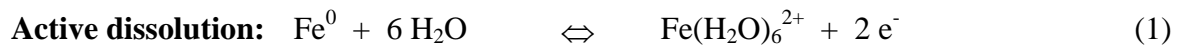
39 The use of  $\text{Fe}^0$ -based alloys (zerovalent iron,  $\text{Fe}^0$  materials or  $\text{Fe}^0$ ) is based on the premise,  
40 that quantitative contaminant removal in  $\text{Fe}^0/\text{H}_2\text{O}$  systems is mostly due to contaminant  
41 reduction through electrons from the metal body (direct reduction) [28,29]. Because of the  
42 electrochemical nature of aqueous iron corrosion [30], this is only possible at the  $\text{Fe}^0$  surface  
43 or at the surface of an overlaying electrically conductive oxide-film (e.g.  $\text{Fe}_3\text{O}_4$ ). However,  
44 given that under typical ranges of sub-surface pH ( $6 \leq \text{pH} \leq 9$ ) there are several possible  
45 contaminant removal mechanisms (adsorption, co-precipitation, precipitation) in  $\text{Fe}^0/\text{H}_2\text{O}$   
46 systems, it is doubtful whether direct reduction may significantly contribute to contaminant  
47 removal as it is currently accepted – and repeated in the introduction of many articles/books.  
48 For the sake of clarity, it should be stated that contaminant reduction is not a stand-alone  
49 removal mechanism as reduction products must be removed from the aqueous phase.

50 The objective of the present communication is to recall the instability of the concept of direct  
51 reductive contaminant removal through  $\text{Fe}^0$  in  $\text{Fe}^0/\text{H}_2\text{O}$  systems which is currently the main  
52 prop that holds up the iron reactive barrier technology. The study is based on a literature

53 review on the process of iron corrosion and the reductive properties of Fe<sup>II</sup> species and H/H<sub>2</sub>.  
54 It is shown that quantitative contaminant removal can only occur within the film of corrosion  
55 products (oxide-film) at the vicinity of the Fe<sup>0</sup> surface. The process of iron corrosion will first  
56 be presented, followed by a discussion of the contaminant interactions within the oxide-film  
57 and two strong arguments against direct reduction through Fe<sup>0</sup> materials.

## 58 2 The Process of Aqueous Iron Corrosion: Oxide-film Generation

59 Under aqueous conditions elemental iron (Fe<sup>0</sup>) may dissolve (solvation) to an oxidized Fe<sup>II</sup>  
60 specie (active dissolution or corrosion) according to Eq. (1), or form a second phase film –  
61 usually an insoluble 3D surface oxide-film (passivation) – according to Eq. (2):



62 Active dissolution and passivation are competing reactions. An oxide-film will form  
63 whenever the metal solubility is low (circumneutral pH values – Fig. 1). The further active  
64 metal dissolution (corrosion) depends on the protectiveness of the generated oxide-film.  
65 Whether a film is protective or not primarily depends on the relative unit-cells (packing  
66 distances or lattice parameters a, b, c, see Tab. 1) of the metal and its oxides [33,34]. In the  
67 case of iron, the unit-cells of the elemental metal and its oxides are not particularly close  
68 (Tab. 1); thus there is no tendency for an iron oxide-layer (oxide-film) to adhere to metallic  
69 iron (Fe<sup>0</sup>). Therefore, an oxide-film instantaneously forms but is constantly flaked off and  
70 exposes fresh iron surface to the environment [33,34]. Iron corrosion will normally continue  
71 until the material is depleted.

72 The formation of an oxide-film on a Fe<sup>0</sup>-material upon aqueous corrosion is characteristic for  
73 pH > 4.5 [35,36] and further depends on several parameters: reactivity of the underlying Fe<sup>0</sup>-  
74 material, temperature, composition, and water flow velocity. These parameters determine the  
75 structure, the thickness and the porosity of the generated film. Such films grow by counter  
76 migration of Fe<sup>II</sup> species from the Fe<sup>0</sup> surface (outward migration) and H<sup>+</sup>, O<sub>2</sub>, and other

77 solutes from the flowing water (inward migration).  $\text{Fe}^{\text{III}}$  species are generated, they migrate,  
78 precipitate and are possibly reduced within the oxide-film. The driving forces for species  
79 transport are mostly electromigration (ionic species) and concentration gradients (all species).  
80 The reaction scheme for film formation can be divided into four steps [37]: (i) active  
81 dissolution (Eq. 1), (ii) transition range, (iii) pre-passive range, and (iv) oxide-film formation.  
82 In the transition and pre-passive range the metal becomes progressively covered by  $\text{Fe}(\text{OH})_2$   
83 and/or  $\text{Fe}(\text{OH})_3$  adsorbates. These adsorbates increasingly retard the active dissolution. The  
84 oxide-film is subsequently formed when the  $\text{Fe}^0$  is completely covered with  $\text{Fe}(\text{OH})_2$  /  
85  $\text{Fe}(\text{OH})_3$  and deprotonization leads to the formation of a layer of iron oxide and  
86 oxyhydroxides (iron oxides:  $\text{FeOOH}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4\dots$ ). It is very important to note that, once  
87 formed, the oxide-film should not be considered as a rigid layer, but instead as a system in  
88 dynamic equilibrium between film dissolution and film growth [37]. In other words, the  
89 oxide-film can adjust its composition and thickness to changing environmental factors (time,  
90 groundwater composition, temperature, microbial activity). In particular, the presence of some  
91 components (e.g.  $\text{PO}_4^{3-}$ ) in groundwater may favour the production of insoluble corrosion  
92 products, possibly leading to an impervious and tenacious oxide-film. The corrosion reaction  
93 becomes self-limiting, as the corrosive medium can no longer diffuse through the oxide-film.  
94 Other groundwater components (e.g.  $\text{Cl}^-$ ), will disturb the formation of continuous oxide-films  
95 or increase their porosity [38]. In this case  $\text{Fe}^0$  active dissolution will continue until the  
96 material is depleted.

97 As already discussed,  $\text{Fe}^0$  materials own their suitability for groundwater remediation to the  
98 fact that the oxide-film continually flakes off and exposes the  $\text{Fe}^0$  surface to the corrosive  
99 aqueous environment. However, new films are suddenly generated such that the bare  $\text{Fe}^0$   
100 surface is not accessible for contaminants as a rule. In fact, all contaminants (organic and  
101 inorganic) interact more or less strongly with the overlaying iron oxides [39]. The next  
102 section will discuss some of these interactions.

### 103 3 Contaminant/Oxide-Film Interactions in Fe<sup>0</sup>/H<sub>2</sub>O Systems

104 As shown clearly, in a Fe<sup>0</sup>/H<sub>2</sub>O system an interface Fe<sup>0</sup>/H<sub>2</sub>O does not exist as a rule [17,35,  
105 40-42], but rather two interfaces: (i) Fe<sup>0</sup>/oxide-film, and (ii) oxide-film/H<sub>2</sub>O. Even though the  
106 metal surface may be temporally accessible at locations where the oxide-film is discontinued  
107 [40], this can not be a rule. With these rare exceptions, to reach the Fe<sup>0</sup> surface, any  
108 contaminant must find its way across the oxide-film. Therefore, investigations regarding  
109 contaminant removal in Fe<sup>0</sup>/H<sub>2</sub>O systems should always be conducted under conditions  
110 favouring the generation and the transformation of an oxide-film (ideally stagnant conditions,  
111 see below).

112 In a Fe<sup>0</sup>/H<sub>2</sub>O system, a contaminant may be subject to four types of reactions: adsorption  
113 (physical and chemical), co-precipitation, oxidation and reduction. Oxidation reactions are not  
114 further considered in this communication. However, it is considered that oxidation products  
115 must be removed from the aqueous phase by adsorption, co-precipitation, precipitation or  
116 volatilization. Three different reduction pathways were specified [21,43,44]: (i) direct electron  
117 transfer from iron metal (direct reduction), (ii) catalyzed reduction by molecular H<sub>2</sub> (or atomic  
118 H) from H<sub>2</sub>O reduction; the reaction is catalyzed by the Fe<sup>0</sup> surface or the Fe oxyhydroxides  
119 surface, (iii) catalyzed reduction by structural or dissolved Fe<sup>II</sup> at the Fe oxyhydroxides  
120 surface (Fe<sup>II</sup> derived both from iron corrosion and from oxide dissolution). Therefore,  
121 potential roles of the oxide-film include [41,45]: (a) serving as an electron and ion transport  
122 barrier, hence reduction of solutes may occur primarily at pits or similar defects; (b) behaving  
123 as a conductor or semiconductor, which allows charge to pass across the interface with some  
124 resistance; (c) functioning as a catalyst, where adsorbed Fe<sup>II</sup> (and H/H<sub>2</sub>) provides strongly  
125 reducing surface sites, and (d) serving as Fe<sup>II</sup> source whereas Fe<sup>III</sup> oxides are reduced  
126 chemically (e.g. by H<sub>2</sub>) or biologically.

127 The redox reactivity of a Fe<sup>0</sup>/H<sub>2</sub>O system is believed to primarily depend on the chemical  
128 thermodynamics of the two redox-systems of iron [46]: Fe<sup>II</sup>/Fe<sup>0</sup> ( $E^0 = -0.44$  V) and Fe<sup>III</sup>/Fe<sup>II</sup>

129 ( $E^0 = 0.77$  V). Therefore, the aim of using  $Fe^0$  in groundwater remediation under anoxic  
130 conditions has been to exploit the negative potential of the couple  $Fe^{II}/Fe^0$  to degrade or  
131 immobilize redox-labile contaminants (direct reduction). However, dissolved ferrous iron  
132 from the  $Fe^{III}/Fe^{II}$  redox couple can act as reductant for soil components (e.g.  $MnO_2$ ) and  
133 contaminants (indirect reduction 1). Furthermore, it has been shown that adsorbed or  
134 structural  $Fe^{II}$  (structural  $Fe^{III}/Fe^{II}$ :  $-0.34 \leq E^0(V) \leq 0.65$ ) can be more powerful in reducing  
135 contaminants [47] (indirect reduction 2) than the  $Fe^0$  surface ( $E^0 = -0.44$  V). On the other side  
136 recent results from Strathmann and co-workers [48] demonstrated that, when complexed with  
137 organic substances, aqueous  $Fe^{II}$  (dissolved organic  $Fe^{III}/Fe^{II}$ :  $0.520 \geq E^0(V) \geq -0.509$ ) is  
138 significantly more powerful than aqueous  $Fe^{II}$  ( $E^0 = 0.77$  V) (indirect reduction 3). Therefore,  
139 abiotic contaminant reduction in a  $Fe^0/H_2O$  system does not necessarily take place by  
140 reduction through electron from  $Fe^0$  (direct reduction). It is to keep in mind that this  
141 discussion considered molecular ( $H_2$ ) and atomic (H) hydrogen as potential reducing agents  
142 without considering further details on the reaction mechanism.

143 Contaminant migration through an oxide-film to the  $Fe^0$  surface may be a process which is  
144 limited by size exclusion effects [49]. Since contaminants are mostly larger than  $H_2O$  in their  
145 molecular sizes, in extreme cases, inner layers of the film may only be accessible to protons  
146 ( $H^+$ ) and water molecules ( $H_2O$ ). Consequently, with decreasing porosity, iron is corroded  
147 merely by water ( $H_2O$  or  $H^+$ ). Even under external (groundwater) oxic conditions oxygen may  
148 deplete completely within the oxide-film (e.g. through oxidation of  $Fe^{II}$ , as discussed above)  
149 [50]. In this case, contaminant reduction can only be the result of structural  $Fe^{II}$  or hydrogen  
150 (H or  $H_2$ ) activity in the oxide-film or at the film surface. The reaction products remain  
151 adsorbed or are dissolved in groundwater depending on their relative affinity to iron oxides  
152 and groundwater chemistry.

153 Besides the molecular size of contaminants, their interactions with iron corrosion products  
154 ( $Fe^{II}$ -species,  $H/H_2$ ) and the body of the transforming oxide-film are important. Since the

155 oxide-film is a good adsorbent for both contaminants and  $\text{Fe}^{2+}$  ions (resulting in more reactive  
156 structural  $\text{Fe}^{\text{II}}$ ), contaminant reduction will certainly occur at the meeting point within the  
157 oxide-film, more or less far from the  $\text{Fe}^0$  surface. In fact,  $\text{Fe}^{2+}$  ions from  $\text{Fe}^0$  oxidation migrate  
158 in the direction of increasing pore sizes and contaminants in the opposite direction [51]. In all  
159 the cases quantitative contaminant reduction at the surface of  $\text{Fe}^0$  is not likely to occur.  
160 Furthermore, irrespective of any interactions between contaminant and film materials (non-  
161 specific mechanism) [52], a contaminant can be entrapped in the matrix of precipitating and  
162 growing oxide-films (co-precipitation). A co-precipitated contaminant can not further migrate  
163 to the  $\text{Fe}^0$  surface. Such species will remain adsorbed and can be reduced by diffuse  $\text{H}/\text{H}_2$  or  
164  $\text{Fe}^{\text{II}}$ . Even physically adsorbed contaminants may be reduced within the oxide-film because of  
165 diffusion hindrances and the thermodynamic favorable catalytic reduction through  $\text{H}/\text{H}_2$  or  
166  $\text{Fe}^{\text{II}}$ . This affirmation is valid irrespective from the conductive properties of the oxide-film.  
167 Remember that direct reduction within or at the surface of the film is only possible if the  
168 oxide-film is electrically conductive. But even electrically conductive magnetite-layers, may  
169 passivate  $\text{Fe}^0$  if they inhibit the migration of  $\text{Fe}^{2+}$  away from the surface.

170 This discussion reiterates that the formation of oxide-films at  $\text{Fe}^0$  surfaces is an inherent  
171 process of aqueous iron corrosion under environmental conditions. Depending on the film  
172 thickness, its porosity and its interactions with individual contaminants, an oxide-film can act  
173 as a diffusion barrier, a reactive barrier and/or as a molecular sieve hindering or lowering  
174 contaminant access to  $\text{Fe}^0$  surfaces [50,53]. Therefore, mechanistic investigations regarding  
175 contaminant removal by  $\text{Fe}^0$  materials should be accomplished under conditions favoring  
176 surface oxide-film generation and transformation [51]. On the contrary, the large majority of  
177 reported  $\text{Fe}^0$  mechanistic results from batch experiments were achieved under well-mixed  
178 conditions. Under these experimental conditions however, (i)  $\text{Fe}^0$  dissolution is accelerated,  
179 yielding to more corrosion products which may adsorb contaminants or immobilize them  
180 during their transformation (e.g., precipitation, recrystallization). Thus, increased generation

181 of corrosion products complicates mechanistic investigations; (ii) corrosion products  
182 precipitation (oxide-film formation) in the vicinity of  $\text{Fe}^0$  surface is avoided or delayed since  
183  $\text{Fe}^{\text{II}}$  transport away from the surface is accelerated; and (iii) chemical dissolution and  
184 mechanical abrasion of oxide-films is possible.

#### 185 **4 Low Reactivity of Iron Metal under Environmental Conditions**

186 Iron-based alloys for environmental remediation have been originally introduced for the  
187 reduction of halogenated organic compounds [20,21,54]. Initial encouraging results prompted  
188 researchers to extend their applicability to a large array of organic and inorganic compounds  
189 [12,15,55-57]: Thereby, key features characterizing the reactivity of  $\text{Fe}^0$  materials under  
190 environmental conditions have been overseen. Three examples for illustration:

191 • Beside catalytic hydrogenation many reductive agents have been successfully used in  
192 the synthetic organic chemistry. The most classic and practical reductants are zinc ( $\text{Zn}^0$ ), tin  
193 ( $\text{Sn}^0$ ), and iron ( $\text{Fe}^0$ ) [58]. However, the reactions with  $\text{Fe}^0$  are performed in organic solvents  
194 or in aqueous acidic solutions (**statement 1**). This statement suggests that using  $\text{Fe}^0$  materials  
195 for quantitative contaminant reduction under environmental pH conditions ( $6 \leq \text{pH} \leq 9$ ) is  
196 questionable.

197 • While using elemental metals in the synthetic organic chemistry, it is well-known that  
198 the reactivity of metallic zinc ( $E^0 = -0.763 \text{ V}$ ) is superior to that of iron ( $E^0 = -0.440 \text{ V}$ ) [46].  
199 Therefore, to perform the reduction of some compounds (e.g., nitro compounds to amines)  
200 with  $\text{Fe}^0$ , the reaction should be carried out at higher temperature [58] (**statement 2**).  
201 Statement 2 suggests that using  $\text{Fe}^0$  materials for quantitative contaminant reduction under  
202 ambient temperatures ( $T < 30 \text{ }^\circ\text{C}$ ) is questionable.

203 • Because of the poor solubility of most organic compounds in water at ambient  
204 temperature, the remarkable properties of water near its critical point ( $T_c = 374 \text{ }^\circ\text{C}$ ,  $P_c = 221$   
205 bar) have prompted researchers to use it in organic synthesis [58,59]. There are increasing  
206 numbers of papers which suggest that near-critical water is an excellent solvent for organic



207 reactions because organic reactions in it offer many advantages over those in traditional  
208 organic solvents or acidic aqueous solutions [59] (**statement 3**). Statement 3 corroborates the  
209 conclusions of statement 1 and 2.

210 Altogether statement 1 through 3 clearly show that direct quantitative organic contaminant  
211 reduction through  $\text{Fe}^0$  materials is not likely to occur. Additionally, working under critical  
212 conditions [58] or in acidic aqueous conditions has not univocally elucidated the real reaction  
213 mechanism (hydrogenation by  $\text{H}_2$  or direct reduction by  $\text{Fe}^0$ ). Therefore, before proposing  
214 direct “reductive transformation” as the main pathway of organic compounds removal in  
215  $\text{Fe}^0/\text{H}_2\text{O}$  systems (under atmospheric conditions), the pioneers of the iron barrier technology  
216 should have brought clarity on the key issues of statements 1 and 2. Instead of that, the  
217 voluminous literature on  $\text{Fe}^0$  in the synthetic organic chemistry has been ignored. Even very  
218 well-documented results have been contradicted, one of the most important been without  
219 doubt the reported quantitative reduction of aromatic azo compounds by  $\text{Fe}^0$  materials  
220 [44,60,61]. This reaction (Béchamp reduction) has been investigated more than 150 years ago  
221 by Antoine J. Béchamp [62] and is known to take place in a  $\text{Fe}^0/\text{HCl}$  system [63].

222 Beside the low  $\text{Fe}^0$  reactivity under environmental conditions, inappropriate experimental  
223 conditions are other error sources in investigations regarding the processes of contaminant  
224 removal in  $\text{Fe}^0/\text{H}_2\text{O}$  systems. The next section will present parameters influencing  $\text{Fe}^0$   
225 reactivity and show how too large  $\text{Fe}^0$ /contaminant molar ratios in combination with mixing  
226 operations may have created unrealistic reducing conditions.

## 227 **5 Inappropriate Experimental Conditions**

228 Factors affecting  $\text{Fe}^0$  reactivity can be divided into three subgroups: (i) material-dependant  
229 factors (mostly not directly accessible to researchers), (ii) environment-dependant factors  
230 (investigable at individual relevant sites), and (iii) operational experimental parameters  
231 (should be designated to mimic environment-dependant factors).

232 Material-dependant factors include: manufacturing history of Fe<sup>0</sup> materials, elemental  
233 composition of Fe<sup>0</sup> materials (alloying elements: C, Cr, Mn, Ni, P, S, Si...), Fe<sup>0</sup> particle size  
234 (nm, µm, mm), Fe<sup>0</sup> surface area, and the oxidation state of the Fe<sup>0</sup> surface [11,12]. Centuries  
235 of investigations on iron corrosion have not clarified the relative importance of the individual  
236 factors [3, 34,64,65].

237 Among environment-dependant factors, the following can be enumerated: water flow  
238 velocity, character of the generated oxide-film on Fe<sup>0</sup> (composition, porosity, thickness), the  
239 ambient temperature, the water composition (major ions, co-contaminants), the availability of  
240 molecular oxygen (oxic vs. anoxic conditions), the nature of the contaminant. Environment-  
241 dependant factors are site specific and may significantly vary periodically (e.g. daily,  
242 seasonally). Their profound knowledge is indispensable for the rational choice of operational  
243 experimental parameters. For example the hydrodynamic of the system should reflect the  
244 groundwater flow velocity. This condition is partly considered in designing column  
245 experiments [4], but is almost totally ignored in the design of batch experiments as discussed  
246 above [17,51].

247 Experimental operational parameters are fully determined by individual investigators. Ideally,  
248 their choice should always be rationalized by real situations or by the objective of individual  
249 experiments. These factors include [3,66-68]: Fe<sup>0</sup> preparation (e.g., acetone or acid wash),  
250 buffer application, the molar ratio of Fe<sup>0</sup> to contaminant (Fe<sup>0</sup> mass loading and initial  
251 contaminant concentration), volume of the bottles used in the experiment, volume of model  
252 solution added, mixing operations (bubbling, shaking, stirring), geometry of the reaction  
253 vessel, experimental duration or reaction time. Due to the lack of a unified procedure for  
254 conducting contaminant removal tests in Fe<sup>0</sup>/H<sub>2</sub>O systems, different mechanisms for the same  
255 contaminant can be found in the literature [69,70].

256 From isolated sets of experiments, a huge number of variables (partly enumerated above)  
257 have been shown to affect aqueous Fe<sup>0</sup> reactivity. This suggests that it is practically

258 impossible to correlate data obtained with different natural waters (or synthetic solutions) on  
259 different  $\text{Fe}^0$  samples. Fortunately, however, while each of these factors is undoubtedly  
260 important under some particular set of conditions, there are wide ranges of conditions within  
261 which comparatively few variables have any large effect on  $\text{Fe}^0$  reactivity [36]. In particular,  
262 the main factors in the aqueous iron corrosion in natural waters are: (i) the protectiveness of  
263 films of corrosion products, and (ii) the rate of oxidant diffusion (including  $\text{H}_2\text{O}$ ,  $\text{O}_2$ ,  $\text{H}^+$ ).  
264 Accordingly, any investigation on processes in  $\text{Fe}^0/\text{H}_2\text{O}$  systems should have been conducted  
265 under conditions favouring the formation and the transformation of oxide-films (e.g. in the  
266 mass transfer controlled regime). Ideally, this is obtained under stagnant conditions [51,71].  
267 The discussion above reveals that the failure to consider  $\text{Fe}^0/\text{H}_2\text{O}$  systems as a dynamic  
268 system consisted of the  $\text{Fe}^0$  material underlying a layer of corrosion products (oxide-film) is  
269 one of the major reasons why, despite two decades of intensive laboratory investigations,  
270 several aspects of contaminant removal from aqueous solutions in  $\text{Fe}^0/\text{H}_2\text{O}$  systems are not  
271 really understood. Another important point is the  $\text{Fe}^0/\text{contaminant}$  molar ratios. In the  
272 synthetic organic chemistry, used  $\text{Fe}^0/\text{educt}$  molar ratios are rarely larger than 10 [29]: For  
273 example, Wang et al. [58] found that a ratio of nanosized iron metal to p-nitrotoluene of 3:1  
274 was sufficient for satisfactory results (stirring conditions, 210 °C and 2 h). In the reactive  
275 barrier literature  $\text{Fe}^0/\text{contaminant}$  ratios up to 20,000 [29 and ref. therein] are used without  
276 justification and the solutions are mixed more or less strongly for hours or days.  
277 While using inappropriate mixing operations and too large  $\text{Fe}^0/\text{contaminant}$  ratios, reducing  
278 conditions may have been generated and investigated by means of sophisticated experimental  
279 designs. These conditions are, however, irrelevant for natural systems. Moreover,  
280 geochemical models have been developed for contaminant removal in  $\text{Fe}^0/\text{H}_2\text{O}$  systems while  
281 assuming reductive transformation at the  $\text{Fe}^0$  surface [72]

## 282 **6 Discussions**

283 It has been considered for almost two decades that the use of  $\text{Fe}^0$  materials for groundwater  
284 remediation is based on scientific principles [73-76]. Thereafter, the suitability of  $\text{Fe}^0$   
285 materials for contaminant reductive removal is based on the low redox potential of the couple  
286  $\text{Fe}^{\text{II}}/\text{Fe}^0$  making  $\text{Fe}^0$  a powerful reducing agent for many soluble contaminants [21,77]. But  
287 these considerations are proved instable because the pioneer works on contaminant reductive  
288 removal by  $\text{Fe}^0$  materials did not test and prove their theories by any scientific criteria [75,  
289 76]. In particular the thermodynamics of hydroxide precipitation or Fe solubility were not  
290 properly considered (Fig. 1) [73]. Fortunately, contaminants are successfully removed in  
291  $\text{Fe}^0/\text{H}_2\text{O}$  systems by other processes [73,74]. The rational investigation of these processes and  
292 their optimisation is a challenge for the scientific community [78,79].

293 The instable premise of direct contaminant reduction by  $\text{Fe}^0$  materials upon which the iron  
294 reactive barrier technology is based, has dragged a part of the environmental science  
295 community deeper into confusion during the past decade. For example, in their efforts to  
296 rationalize the removal of uranium (VI) from the aqueous phase in the presence of  $\text{Fe}^0$ , Gu et  
297 al. [80] worked with clearly over-saturated U(VI) solutions (up to 10,000 mg/L or 0.042 M at  
298 near-neutral pH values) and reported that “results from the batch adsorption and desorption  
299 and from spectroscopic studies indicate that reductive precipitation of U on  $\text{Fe}^0$  is the major  
300 reaction pathway”. Under their experimental conditions however, U(VI) precipitation is  
301 thermodynamically and kinetically more favourable than the discussed mechanisms  
302 (adsorption and reduction). Clearly, all has been done to support the questionable premise.

303 Here are three further examples: (i) very well-established scientific results have been  
304 contradicted (e.g. Béchamp reaction) [29]; (ii) contaminant co-precipitation with  $\text{Fe}^{\text{II}}$  and  $\text{Fe}^{\text{III}}$   
305 species which is the principle of flotation [81-86] has been ignored in order ‘to force’ direct  
306 reduction of metallic species to occur; (iii) the well-known “physical barrier” function of  
307 oxide-films has been transformed to that of “mediator of electron transfer” (electron-shuttle)  
308 from underlying  $\text{Fe}^0$  to overlying contaminants (semiconductor and/or coordinating surface)

309 in order to rationalize the hypothetical electron transfer from  $\text{Fe}^0$  surface to dissolved oxidants  
310 [41].

311 The present work and related works [29,51,71,87] have presented a more simple and realistic  
312 model, acknowledging that quantitative contaminant removal primary occurs via adsorption  
313 or co-precipitation within the oxide-film. Depending on the availability of reductants and/or  
314 micro-organisms the contaminant may be further reduced, irrespective from the conductive  
315 properties of the oxide-film. This model is supported by the known adsorptive properties of  
316 iron oxides [39,88,89], and the fact that biological agents (viruses) [90], arsenic [91], and  
317 electrochemically non-reducible contaminants like Zn [92] are successfully removed from  
318 aqueous solution by  $\text{Fe}^0$  materials (e.g. in  $\text{Fe}^0/\text{H}_2\text{O}$  systems).

## 319 **7 Concluding Remarks**

320 The further development of  $\text{Fe}^0$  bed filtration in general and the reactive wall technology in  
321 particular requires the use of appropriate experimental methodologies (e.g. no vigorously  
322 batch experiments). Available scientific results from two research areas must be properly  
323 exploited: (i) The results of investigations regarding passive film formation on  $\text{Fe}^0$  in neutral  
324 and alkaline aqueous solutions. These investigations aimed at developing a detailed  
325 understanding of the film growth mechanisms, the film structure and composition, and the  
326 kinetics and mechanisms of reduction of iron oxides that form on the  $\text{Fe}^0$  surface [93 and ref.  
327 therein], and (ii) The results of investigations regarding the polymerization of iron via  
328 hydrolysis yielding non-crystalline particles of key importance in the adsorption and transport  
329 of organic or inorganic pollutants [38,81].

330 Finally, the most important feature from the present communication is the solution of the  
331 existing vagueness for the design of  $\text{Fe}^0$  beds [94]. In fact, determining an amount of  $\text{Fe}^0$  and  
332 a bed thickness is no more dependant on a reductive reaction [2,95] but is solely a  
333 characteristic of water flow, water chemistry and  $\text{Fe}^0$  intrinsic reactivity [96-98]. In other  
334 words, the profound understanding of the mechanism of contaminant removal in  $\text{Fe}^0/\text{H}_2\text{O}$

335 systems has simplified bed design [96] and Fe<sup>0</sup> bed is now proposed (or recognized as) a  
336 efficient material for decentralized safe drinking water production [97-100]. Intensive  
337 research as several fronts is needed to transform this vision to reality.

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583

583 **Table 1.** Lattice parameters (a, b, c), structure and density of metallic iron and relevant  
 584 corrosion products (iron oxides). The oxide-film on Fe<sup>0</sup> (rust) is an oxide mixture of  
 585 different crystal structure than iron. Therefore the film is porous and poorly adherent  
 586 (non-protective). Data from ref. [31].

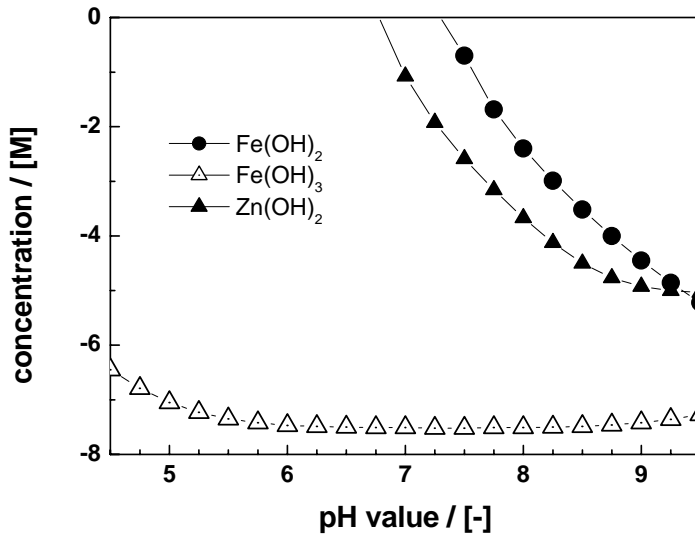
Substance	Structure	Density (g/cm <sup>3</sup> )	lattice parameters (in Å)		
			a	b	c
<b>Fe<sup>0</sup></b>	cubic	7.86	2.866	2.866	2.866
<b>Fe(OH)<sub>2</sub></b>	trigonal	3.40	3.27	3.27	4.62
<b>FeOOH</b> (gel)	cubic		8.37	8.37	8.37
<b>Fe<sub>3</sub>O<sub>4</sub></b> (magnetite)	cubic	5.175	8.396	8.396	8.396
<b>FeOOH</b> (goethite)	orthorhombic	4.28	4.60	10.01	3.04
<b>FeOOH</b> (akageneite)	tetragonal	3.55	10.52	10.52	3.028
<b>FeOOH</b> (lepidocrocite)	orthorhombic	4.09	3.65	12.50	3.07
<b>Fe<sub>2</sub>O<sub>3</sub></b> (hematite)	trigonal		5.035	13.72	5.26

587

588



588 **Figure 1:** pH dependence of metal hydroxide solubilities at pH values of natural waters. The  
589 trend for iron precipitation under oxic conditions ( $\text{Fe}^{\text{II}}$ ) is clear and delineates the suitability of  
590  $\text{Fe}^0$  for water treatment by adsorption and co-precipitation. Even under anoxic condition  
591  $\text{Fe}(\text{OH})_2$  polymerize and readily precipitate. Data from ref. [32]  
592



593