1   **Metallic iron for water treatment: A critical review**

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9

10   **Abstract**

11   Water treatment with metallic iron (Fe^0) is still based on the premise that Fe^0 is a reducing agent.

12   An alternative concept stipulates that contaminants are removed by adsorption, co-precipitation

13   and size-exclusion in a reactive filtration process. This article underlines the universal validity of

14   the alternative concept. It is shown that admixing non-expansive material to Fe^0 as a pre-requisite

15   for sustainable Fe^0-based filtration systems. Fe^0-based filters are demonstrated an affordable,

16   appropriate and efficient decentralized water treatment technology.

17   **Keywords:** Media filtration, Size-exclusion, Water treatment, Zerovalent iron.

18

1   Introduction

Fe-based alloys (elemental iron, Fe^0 materials or zerovalent iron) have been found to be effective for removing a wide range of compounds from water. Studies on the successful removal of organic and inorganic chemicals [1-16] and pathogens [17-21] have been widely published and reviewed [22-30]. However, reports on the mechanism of contaminant removal have not been univocal.

For more than a decade reductive transformations (degradation of organics and precipitation of inorganics) have been regarded as the fundamental mechanism of contaminant removal in Fe^0/H_2O systems [3,31-34]. But the literature contains many contradictory findings regarding the processes of aqueous contaminant removal in the presence of Fe^0. Reported discrepancies include the nature of reaction products [35], the extent of contaminant reduction [36,37], the actual reducing agents (Fe^0, Fe^{II} or H/H_2) [12,38] and the relative importance of adsorption and reduction [37]. These conflicting findings suggest that reductive transformations may not be as important as currently considered. Nevertheless, a 'broad consensus' on reductive transformations persists in the literature despite parallel acknowledgment that the real mechanisms of contaminant removal have not yet been completely elucidated [6,24,32-34,39-41].

Recently, a new concept was introduced stating that contaminants are fundamentally adsorbed onto and co-precipitated with insoluble Fe^0 oxides and hydroxides [42,43]. As for any subject on which there is a difference of opinion, it is pertinent to compare the concepts with the hope of finding the truth in the matter.

2   Reduction or adsorption/co-precipitation?

If contaminants are mostly reduced in Fe^0/H_2O systems (**concept 1**), then one should consistently explain why this is possible at the long-term despite the oxide film formation (layer insoluble Fe^0 oxides and hydroxides) and transformation at the surface of Fe^0. It is important to notice in this regard, that the model for oxide film formation, that was compatible with progressive contaminant reduction [23] was proven unrealistic [44].

43   If contaminants are primarily adsorbed and co-precipitated (**concept 2**) within the oxide film, then

44   one must simply sustain iron corrosion to ensure contaminant removal.

45   **Concept 1** gave birth to the iron reactive barrier technology as only reducible species (mostly

46   chlorinated compounds) were considered [1,3,6,31]. However, reaction products for many

47   chlorinated hydrocarbons have not been clearly identified [35,45,46]. Moreover, Fe^0 consumption,

48   oxide film formation on the clean Fe^0 surface, and rise of pH inevitably accompany the removal

49   processes [47-49]. Due to these inherent properties of Fe^0-mediated reactions, the contaminant

50   removal rate should necessarily decrease with increasing Fe^0 consumption yielding contaminant

51   breakthrough. As this was not observed as the rule, **concept 2** is more close to the reality.

52   Therefore, future researchers should follow **concept 2**. That is working on ways and means to

53   sustain Fe^0 reactivity which automatically yields contaminant adsorption and co-precipitation

54   [48,50-54].

55   It is essential to recall that reality (to be found out) is the action of nature under relevant

56   conditions. Accordingly calling a technology 'passive' is not related to 'no action' but no external

57   input of energy. In other words, active technologies need external energy input to initiate/support

58   the action of nature (the reality). The challenge is to find out, how the nature works. Finding out

59   how nature works is knowledge acquisition. The question here is "how are contaminants removed

60   in Fe^0/H_2O systems?"

61   **2.1   Reduction is not a removal mechanism**

62   In water treatment, chemical reactions are used to facilitate contaminant elimination by one or

63   several removal mechanisms [55,56]. Relevant removal mechanisms are: (i) adsorption, (ii) co-

64   precipitation, (iii) precipitation, (iv) size-exclusion and (v) volatilisation. All water treatment

65   methods are based on these five mechanisms.

66   For water treatment at a specific site, it is important to identify the treatment method that is the

67   most suitable: efficient, affordable and applicable. The treatment system that is best for a

68   particular situation depends mostly on the nature and the concentration of contaminants and the

69 operational requirements of the system. As a rule, a combination of treatment methods is more

70 effective. A practical example is the chemical reduction of Cr^{VI} to Cr^{III} at pH value < 4, followed

71 by an increase of the pH to values > 6.0 for which Cr^{III} precipitates as $Cr(OH)_3$.

72 The example of chromium (atomic number: 24) is very illustrative as chromium and iron (atomic

73 number: 26) are two heavy metals. In other words, aqueous Cr^{III} is only quantitatively removed

74 when precipitation is favourable, e.g. at pH > 6.0 [57].

75 **2.2   Iron solubility and contaminant removal**

76 Iron is a potential contaminant for water. Its maximum contaminant level (MCL) is 0.3 mg/L or

77 5.4 µM [58]. Accordingly, while using Fe-based reactive material (e.g. Fe^0, FeS, FeS_2) in water

78 treatment systems, care must be taken for the residual iron concentration to remain below 0.3

79 mg/L. This requirement delineates the importance of pH dependant Fe solubility of the process of

80 contaminant removal (Fig. 1).

81 In Fig. 1, literature experimental data for the solubility curve of $Fe(OH)_3$ and FeS are represented

82 together with the line for the MCL for Fe (5.4 µM) [59,60]. It is seen that Fe^{II} is by far more

83 soluble than Fe^{III} at all pH values. For pH > 5.5, Fe^{II} concentration is at most comparable to MCL

84 suggesting that Fe^0 is only applicable at pH > 5.5. Clearly, if pH ≤ 4.5 (e.g. acid mine drainage),

85 an pH enhancement should precede Fe^0 application. It should be noticed that Fe^0 corrosion is

86 always coupled with a pH increased: H^+ consumption (Eq. 1) or OH^- production (Eq. 2). Thus for

87 systems at pH 4.0-4.5 the technology can be tested [61].

88
$$Fe^0 + 2 H^+ \Rightarrow Fe^{2+} + H_2 \qquad\qquad (1)$$

89
$$Fe^0 + 2 H_2O \Rightarrow Fe^{2+} + 2 HO^- + H_2 \qquad\qquad (2)$$
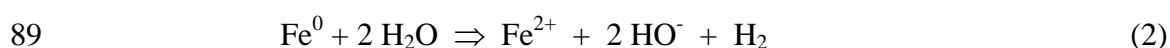
90 Because Fe^0 is oxidized by water (Eq. 2) and water is a solvent a Fe^0/H_2O should be regarded as a

91 zone of precipitating iron oxides and hydroxides [62]. During this precipitation, available foreign

92 species (including contaminants) are inevitably enmeshed in the mass of precipitates (co-

93 precipitation). Resulting precipitates are in turn potential adsorbents for biological and chemicals

94 contaminants. Therefore, adsorption and co-precipitation are definitively the fundamental

95 processes of aqueous contaminant removal in the presence of reactive Fe^0. In a Fe^0 bed, size-

96 exclusion is the third important process ('reactive filtration') [62-65]. A porous bed of granular

97 materials primarily removes dissolved molecules (e.g. size exclusion chromatography) and

98 suspended components (e.g. sand filtration) based on their molecular sizes and shapes. The

99 molecular sieve properties of used (porous) materials is exploited. In all cases volatilisation may

100 occur (if applicable) but chemical precipitation is not likely to occur given that contaminants are

101 usually present in trace amounts [66,67].

102 **2.3   What went wrong?**

103 **2.3.1   The aqueous Fe^0 reactivity**

104 The major problem with the introduction of the Fe^0 remediation technology is that no critical

105 survey of the data available on iron corrosion was done [30,63]. Ideally, the results of such a

106 survey should have been linked for all possible hypotheses. Then well-designed experiments under

107 strictly controlled conditions should have been performed to uncover the observed process of

108 contaminant removal.

109 On the other hand, reactive Fe^0 was tested under the same experimental conditions as inert

110 adsorbents and conflicting results were reported [68-70]. Tested adsorbents included activated

111 carbon, coal, hematite, goethite, lignite, lime, magnetite, peat, sawdust. For example, based on

112 their previous works on the efficiency of several industrial materials for uranium removal [68],

113 Morrison et al. [69] tested Fe^0 and concluded that Fe^0 was the most efficient material for their

114 purpose. In contrast, Indelicato [70] compared Fe^0 and granular activated carbon (GAC) for the

115 removal of chlorinated compounds from groundwater and concluded that GAC was superior to

116 Fe^0. It is obvious, that these articles have overseen the key aspect that the efficiency of Fe^0

117 primarily depends on the (long-term) kinetics of iron corrosion under the experimental conditions.

118 It should be recalled that Fe^0 reactive barriers were primarily designed for large volumes of low

119 contaminated water (micro-pollutants) flowing slowly through Fe^0 beds. Under such conditions,

120 the kinetics of iron corrosion and the residence time of water within the beds may be sufficient to

121 generate enough corrosion products for quantitative contaminant removal. In contrast, the

122 adsorptive capacity of adsorbents is maximal at the beginning of the experiment. Provided that the

123 water flow velocity is satisfactory, adsorptive filtration (e.g. GAC) could be efficient where

124 reactive filtration with Fe^0 is not efficient.

125 The key issue is not the relative efficiency but the appropriateness of each class of materials. If

126 this issue is properly addressed, then an appropriate design could be achieved. The results of

127 Miyajima [71] have recently clarified the relationship between 'intrinsic reactivity' and 'removal

128 efficiency'. Summarized, the intrinsic reactivity is an invariable characteristic of a material that

129 does not depend on its amount or the operational conditions. The efficient of a material

130 characterizes the extent to which the material can remove a given contaminant under defined

131 operational conditions. In other words, 'efficiency' and 'reactivity' should never be randomly

132 interchanged.

133 **2.3.2   The origin of the mistake**

134 A careful look on the first 4 peer-reviewed articles on Fe^0 [1-4] (Table 1) suggests that a

135 systematic investigation of all observed phenomena would have avoided the mistake of

136 considering Fe^0 as a reducing agent. For example, the observed time lag for contaminant removal

137 reported by Schreier and Reinhard [4] is consistent with the view that (at pH > 4.5) contaminants

138 are removed by adsorption and co-precipitation (**concept 2**). This time lag thus corresponds to the

139 time necessary for the in-situ production of removing agents (Fe^{II}/Fe^{III} hydroxides and oxides). On

140 the other hand, the necessity to sustain chemical reduction by an addition of pyrite as reported by

141 Lipczynska-Kochany et al. [2] depicted a clear concern that there would be a problem with

142 chemical reduction (e.g. reductive degradation) at pH values relevant for natural waters. It is

143 important to notice that reactive pyrite is added by Lipczynska-Kochany et al. [2] as a long-term

144 pH shifting agent and not as an own-reducing agent as successfully tested for example by

145 Kriegman-King and Reinhard [72,73]. Both these articles [2,4] were almost ignored (less than 70

146 citations each as referred to Table 1) and the idea presented above were not further investigated.

147 The article of Matheson and Tratnyek [3], one of the favoured (Table 1), has recently been granted

148 as *2011 Outstanding Publication Award* from the Association of Environmental Engineering and

149 Science Professors (AEESP). The AEESP is made up of professors in academic programs

150 throughout the world who provide education in the sciences and technologies of environmental

151 protection. In fact, this article [3] is currently among the most cited articles published at

152 *Environmental Science & Technology.* However, the theory propagated by this article is based on

153 a wrong interpretation of good experimental observations as discussed in section 2.1. In other

154 words, the current paradigm for the rationalization of the operating mode of Fe^0/H_2O remediation

155 systems is unstable. Paradigm refers to all knowledge about which there is agreement in science.

156 **2.3.3 The propagation of the mistake**

157 Having met an agreement on a false premise, researchers have been reporting on findings (i)

158 disagreeing 150 years intensive research on aqueous iron corrosion [74-76], (ii) disagreeing good

159 results of synthetic organic chemistry [30], (iii) neglecting the voluminous work available from the

160 hydrometallurgy, and the petroleum industry [75-79], and (iv) not able to explain why non-

161 reducible contaminants are quantitatively removed in Fe^0/H_2O systems [30,42,43]. It is important

162 in this regard to notice that Fe^0 is also used for oxidative conversion of aqueous contaminants [13].

163 However, contaminant oxidation is also not a removal mechanism (section 2.1).

164 Beside the improper consideration of available results from other branches of science two other

165 key factors have contributed to maintain confusion on the mechanism of contaminant removal in

166 Fe^0/H_2O systems: (i) the use of inappropriate experimental conditions and (ii) the failure to use

167 sequential extraction while making mass balances.

168 **2.3.4 Inappropriate experimental conditions**

169 There is actually no standard experimental protocol for the investigation of processes in Fe^0/H_2O

170 systems. Available results are not really comparable [80,81]. In particular the used mixing

171 operations (agitating, shaking, stirring) have disturbed the process of oxide film formation yielding

172 possibly reproducible results under well-designed laboratory conditions. These conditions are

173 however difficult to reproduce in the subsurface [30].

174 **2.3.5 Non-conclusive mass balance**

175 No convincing carbon balances between reactants and products have ever been successfully done

176 for many chlorinated hydrocarbons [45]. This means that organic contaminants that have

177 disappeared from the aqueous phase are mostly considered chemically reduced. The situation is

178 similar for inorganic contaminants for which speciation experiments have been mostly made

179 without efforts to reductively dissolve iron corrosion products [82]. In other words, available

180 results from geochemistry have equally not been properly considered. In fact, reductive dissolution

181 of iron (and manganese) oxides is integral part of all sequential extraction schemes [83-85]. For

182 example, Ma and Rate [84] used ammonium oxalate for amorphous iron/manganese oxides and

183 hydroxylamine hydrochloride for crystalline iron/manganese oxides. As far as the author could

184 ascertain, only Kishimoto et al. [86] have chemically reduced iron corrosion products for

185 mechanistic demonstration. Previous research articles have used reducing agents to demonstrate

186 the stability of removed contaminants [87,88].

187 **3   Discussion**

188 The presentation above has acknowledged that the concept of contaminant reductive

189 transformation as removal mechanism in Fe^0/H_2O is clearly inadequate for explaining many

190 experimental and field observations. Furthermore, irreversible contaminant removal which could

191 result from contaminant co-precipitation with iron corrosion products has been mistakenly

192 regarded as contaminant reductive transformation. However, the actual reactive wall design (e.g.

193 wall sizing) is based on this concept [39,89-91]. Therefore, it is urgent to reconsider available data

194 and models [92,93]. Moreover, further research work should be performed under adequate

195 experimental conditions, including non-disturbed conditions of slow mixing regimes in batch

196 experiments [30,81]. More research under relevant conditions is needed before the concept of

197 contaminant co-precipitation can be fully understood and predicted. Considering its nature, this is

198 a challenge which can only be properly addressed by several research groups.

199 Finally, it must be explicitly said that the concept of contaminant co-precipitation is not a

200 contradiction but an extension of the reductive transformation concept. The new concept explains

201 better why various contaminants are continuously removed in Fe^0/H_2O systems despite

202 "passivation" of the Fe^0 surface [52,94]. Adsorbed and co-precipitated contaminants can be further

203 reduced [42,43]. Based on this knowledge, Fe^0-based filtration systems (including reactive walls)

204 can be better designed [71,93]. The next section presents Fe^0 as a universal material for safe

205 drinking water provision at small scale.

206 **4   Metallic iron for safe drinking water provision**

207 The conventional approach for safe drinking water provision is to treat natural water in a treatment

208 plant and distribute through a pipeline network to the population [95,96]. One of the most severe

209 shortcomings of this approach is that any sudden interruption (e.g. disasters: floods, droughts,

210 quakes, tsunamis, hurricanes) could leave thousands of people without drinking water supply for

211 some days or weeks. There is a current trend for decentralized solutions for safe drinking water

212 supply [56,64,95-98].

213 **4.1   Basic requirements for decentralized water supply solutions**

214 Centralized waterworks are sophisticated systems with high demand of energy, skilled operation

215 personnel and chemicals [55,96,99]. To be applicable worldwide, a water supply system must be

216 (i) efficient, (ii) affordable and (iii) applicable in small and secluded remote areas (including

217 islands) without electricity grid and possibly without (enough) skilled personnel [94,98,100-104].

218 Presently only chlorination, coagulation, filtration, solar disinfection, ceramic filters and biosand

219 filters fulfil these basic criteria [56,103]. However, chlorination and coagulation need skilled

220 personnel and should never be performed by illiterates (e.g. in developing countries). Solar

221 disinfection can not address chemical contamination and the efficiency for both ceramic and

222 biosand filters for virus removal was shown non satisfactory [97]. In other words, there is

223 presently no simple, efficient and affordable technology for water supply in low-income remote

224 communities. One exception is the recently developed "WaterBackpack" at the University of

225 Kassel (Germany) [97]. The "WaterBackpack" is a "small, transportable and easy to use dead-end

226 membrane filtration unit for basic water supply" for small communities in the range of 200 up to

227 500 people [97]. The "WaterBackpack" is suitable for critical situations like natural disasters (e.g.

228 earthquakes, tsunami) or wars (refugee camps). The need for sustainable, affordable safe drinking

229 water technologies for low-income communities persists. Some of these communities have only so

230 few inhabitants (down to less than 10 persons) for who the current version of "WaterBackpack" is

231 not appropriate even though it could be affordable (around Euro 700).

232 **4.2   Concept of Fe^0 for safe drinking water provision**

233 The suitability of metallic iron for decentralized drinking water provision arises from two main

234 reasons: (i) metallic iron is widely available; iron filings can be produced locally even in poor

235 localities (so-called 'indigenous iron') at low-cost or no money expense and (ii) water corrodes

236 Fe^0 to strongly adsorbing iron hydroxides and oxides [49,105-114]. As demonstrated above these

237 iron precipitates should be regarded as collectors in a sand filter [115,116]. Accordingly, biosand

238 filters should be amended with Fe^0 to yield efficient gravity filters. The design of Fe^0 filters has

239 been discussed in several recent articles [52,116] and will not be repeated here.

240 The heart of the Fe^0 filter is a suitable reactive Fe^0 which should be mixed to an inert material (e.g.

241 anthracite, gravel, pumice, sand) or a reactive but not expansive material (e.g. MnO_2, TiO_2) in a

242 reactive zone [53]. The reactive zone should be sandwiched between two biosand filters (BSFs)

243 (Fig. 2) [117]. The first BSF scavenges O_2 and removes pathogens and the second removes

244 dissolved iron from the reactive zone. It can be anticipated that to each Fe^0 (intrinsic reactivity)

245 will correspond a thickness (H_{rz}) of the reactive zone and a thickness (H_{BSF2}) of the second fine

246 sand layer. The concept presented here can be realized at any corner of this world at several scales.

247 With regard on the developing world, this is not a technology transfer in the conventional sense

248   [102], but a 'knowledge sharing' that could enable research institutions in the developing world to

249   solve a long lasting problem by local initiatives.

250   The concept is affordable and applicable because: (i) no chemicals is needed, (ii) no energy is

251   needed (gravity filtration), (iii) no (skilled) operation personnel is needed, and (iv) no intensive

252   maintenance is needed. The sole need is a concept for recycling iron for new filters.

253   **5   Further applications of Fe^0 in environmental remediation**

254   The knowledge, that Fe^0 is used to produce reactive species is not unique to Fe^0 filters. For

255   example, Gould [118] used Fe^0 as reducing agent for Cr^{VI}, but their results demonstrated that more

256   Cr^{VI} is reduced than predicted by the stoichiometry of the reaction between Fe^0 and Cr^{VI}. In this

257   case, Fe^{II} and H_2 are efficient reducing agents for Cr^{VI} (Table 2). In another example, Bafghi et al.

258   [119] used powdered Fe^0 as Fe^{II} generator for the reductive dissolution of MnO_2. Their results

259   showed that Fe^0 is superior to Fe^{II}-bearing materials "as far as dissolution rate and efficiency were

260   concerned". In a third example, Chen et al. [120] positively investigated the potential of nano-Fe^0

261   for hydrogen generation. In a fourth example, Biswas and Bose [121] successfully tested Fe^0 as

262   source of H_2 for autotrophic denitrification. In a fifth example, Fe^0- and Fe^{II}-bearing materials are

263   used as cost-effective oxygen scavengers to protect oxygen-sensitive foods from oxidation [122-

264   124]. The idea is to eliminate or reduce the levels of oxygen inside packs. The working

265   mechanism is the reaction of iron (Fe^0, Fe^{II}) with oxygen in the container to form Fe^{III} oxides

266   [124]. These five examples show clearly that Fe^0 can efficiently be used as parent material to

267   produce useful species for different purposes. In Fe^0/sand filters, Fe^0 is used as generators for

268   colloids which adsorb and/or enmesh contaminants during their precipitation. In other words, Fe^0

269   is used to improve filtration which is basically a size-exclusion process [99]. Accordingly, the

270   removal of very small particles (e.g. viruses) is not guaranteed by small pore sizes like in

271   membrane filtration [97,103] but by the dynamic process of aqueous iron corrosion [47,64,65].

272   The geochemistry of iron in general and the behaviour of iron minerals in soils with regards to

273   contaminant removal [125,126] suggest that Fe^0 can be used as progressive source for slow release

274 of Fe (hydr)oxides in several remediation scenarios [127] Relevant applications include: (i)

275 remediation of contaminated groundwater, (ii) production of safe drinking water, (iii) treatment of

276 industrial and agricultural wastewater, (iv) treatment of hospital effluents, (v) improvement of

277 water quality in aquifers, (vi) improvement of river bank filtration, (vii) treatment of contaminated

278 soils, and (viii) optimisation of artificial aquifer recharge. The material to be used in each

279 application depends on the suitable operational conditions. However, it can be anticipated that a

280 large array of materials with different reactivity should be available. Therefore, a standard

281 protocol for the characterization of the intrinsic reactivity of Fe^0 materials is urgently needed.

282 Depending on their intrinsic reactivity, materials could be classified with respect to their suitable

283 application; e.g. Fe^0 for safe drinking water, Fe^0 for soil treatment, Fe^0 for irrigation water, Fe^0 for

284 drainage water, Fe^0 for river bank filtration…

285 **6   Concluding remarks**

286 The universality of the view that Fe^0 is not a reducing agent is delineated. Regarding Fe^0 as a

287 generator of 'contaminant collectors' [116] has enabled the conceptual design of Fe^0-amended

288 slow sand filters (Fe^0 SSFs) which are yet to be realized. A Fe^0 SSF has a large potential for

289 application to small-scale systems, in particular in low-income communities worldwide: (i) it is

290 totally chemistry free, (ii) it is simple to design, (iii) it is easy in operation and maintenance, (iv) it

291 is cost effective and (v) it is reliable upon proper design. Innovative designs of the reactive zones

292 (e.g. use of Fe^0-composites, Fe^0/MnO_2, Fe^0/pumice) will increase the sustainability of Fe^0 filtration

293 beds [54,128].

294 Intensive research with column and pilot studies are necessary to verify and optimise the presented

295 concept. In this effort, the proper consideration of the volumetric expansive nature of iron

296 corrosion should be carefully considered. In particular, lowering the concentration of dissolved O_2

297 at the inlet of the filter is a key issue (Table 3). The proper disposal of spent media as well as the

298 recycling of used materials should be considered during the testing stage.

299   The knowledge that Fe^0 is not a reducing agent is also essential for the further development of the

300   iron wall technology for groundwater remediation. In fact, considering the volumetric expansive

301   nature of iron corrosion [74,76,129,130], the question as whether mixing Fe^0 and inert materials

302   (e.g. gravel, sand) is beneficial or not [40,71, 131-133] is now definitively solved. Mixing Fe^0 and

303   non-expansive materials is even a pre-requisite for system sustainability [134]. Accordingly, a

304   reactive wall containing a zone with 100 % Fe^0 is not viable. Consequently, the rationale for the

305   sustainability of reactive walls with a pure Fe^0 layer [24,27,66] is yet to be elucidated. A plausible

306   explanation is that used materials were not very reactive. In such a constellation the reactivity of

307   the wall could be sustained by an array of abiotic and biotic reductive reaction recycling Fe^{III} to

308   Fe^{II} [135]. The impact of chemical reaction within the barrier is the progressive generation of

309   colloids for contaminant 'collection'. Without recycling, Fe^{II}/Fe^{III} colloids are irreversibly

310   transformed to less/non reactive crystalline forms [134,136-138]. As regarding the failure cases

311   [66,70,139,140], it can be anticipated that used materials were very reactive under site specific

312   conditions. Verifying this hypothesis is a challenge for the scientific community and an

313   opportunity to further develop the already established remediation technology.

314   **Acknowledgments**

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645

645 **Table 1**: Overview on important results of the four first published peer-reviewed articles on the

646 Fe^0/H_2O system in 1994 and the number of their citations in Scopus (2012/09/10). [X stands for

647 contaminant; RCl is a chlorinated hydrocarbon].

648

Reference	Systems	X	Findings	Citations
Matheson et al. [2]	Fe^0/H_2O	CH_xCl_y	Degradation mostly by Fe^0	682
Gillham et al. [1]	Fe^0/H_2O	RCl	Enhanced degradation	650
Schreier et al. [4]	Fe^0/H_2O	C_2Cl_4	Partial degradation with lag time	70
Lipczynska-Kochany [3]	$Fe^0/FeS_2/H_2O$	CCl_4	FeS_2 sustains degradation	56

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651

651   **Table 2.** Some relevant reactions involved in Cr^{VI} removal in the system Fe^0/H_2O. It can be seen

652   that Fe^0 and its both secondary reaction products (Fe^{2+}, H_2) can reduce Cr^{VI}. Fe^0 is

653   oxidized by water (H^+), Fe^{3+}, dissolved O_2 and Cr^{VI}. Ternary reaction products (FeOOH,

654   Fe_3O_4, Fe_2O_3) are involved in the process of Cr removal (adsorption). Whether reduced

655   or not Cr is enmeshed in the mass of Fe precipitates or adsorbed at their surface.

656

Reaction equation		E^0	Eq.
		(V)	
Fe^0	$\Leftrightarrow Fe^{2+} + 2\ e^-$	-0.44	(1)
$2\ H^+ + 2\ e^-$	$\Leftrightarrow H_2$	0.00	(2)
$Fe^{3+} + e^-$	$\Leftrightarrow Fe^{2+}$	0.77	(3)
$O_{2(aq)} + 2\ H_2O + 4\ e^-$	$\Leftrightarrow 4\ OH^-$	0.81	(4)
$CrO_4^{2-} + 8\ H+ + 3\ e^-$	$\Leftrightarrow Cr^{3+} + 4\ H_2O$	1.51	(5)
$Fe(OH)_3$	$\Rightarrow \alpha\text{-},\ \beta\text{-FeOOH},\ Fe_3O_4,\ Fe_2O_3$		(6)*
$FeOOH + Cr^{VI}_{(aq)}$	$\Rightarrow FeOOH\text{--}Cr^{VI}_{(adsorbed)}$		(10)

657   *non stoichiometric

658

658   **Table 3**: Coefficient of volumetric expansion (η) of relevant iron species. The reference ($\eta = 1$) is

659   Fe^0 with a molar volume (V_m) of 7.6 cm^3/mol. x_{Fe} is the stoichiometry of Fe in the solid phase. It

660   is seen that the largest volumetric expansion occurs under oxic conditions ($\eta = 4.53$ for ferric

661   hydroxide). V_m values are adopted from Henderson and Demond [66].

662

Solid phase	Name	V_m	x_{Fe}	η	η
		(cm^3/mol)	(-)	(-)	(%)
Fe^0	Iron metal	7.6	1.0	1.00	0
$FeOOH$	Goethite	20.3	1.0	2.67	167
$Fe(OH)_2$	Ferrous hydroxide	26.4	1.0	3.47	247
Fe_2O_3	Maghemite	29.1	2.0	1.91	91
$FeCO_3$	Siderite	29.3	1.0	3.86	286
Fe_2O_3	Hematite	30.1	2.0	1.98	98
$Fe(OH)_3$	Ferric hydroxide	34.4	1.0	4.53	353
Fe_3O_4	Magnetite	45.0	3.0	1.97	97
$Fe^{II}_4Fe^{III}_2(OH)_{12}CO_3.2H_2O$	Carbonate green rust	176.3	6.0	3.87	287

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666

Figure Caption

667

668 **Figure 1**: Comparison of the solubility limit of iron with the EPA maximum contaminant level

669 (0.3 mg/L or 5.4 μM). Data for Fe^{III} solubility (0.01 M NaCl at 25°C) are from Liu and

670 Millero [59] while data for Fe^{II} solubility are from Rickard [60]. Although the

671 experiments are performed under different conditions, it can be seen that iron solubility

672 is minimal between pH 5.5 and 10. This is necessarily the pH range of water treatment

673 using Fe^0 and other Fe-bearing materials.

674 **Figure 2**: Schematic diagram of a three compartments Fe^0-amended biosand filter (BSF). The first

675 and the third columns are conventional BSF. The thickness of column 2 (reactive zone)

676 depends on the intrinsic reactivity of used Fe^0 (after ref. [117])

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