

# 1                   **The Suitability of Metallic Iron for Environmental Remediation**

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## 6    **Abstract**

7    Aqueous contaminant removal in the presence of metallic iron is often regarded as a reductive  
8    transformation mediated by the  $Fe^0$  surface. However, successful removal of theoretically  
9    non-reducible contaminants has been largely reported. This paper presents a rebuttal of the  
10   concept of contaminant reductive transformation. It is argued through a careful examination  
11   of the evolution of the volume and adsorptive properties of iron and its corrosion products  
12   that contaminants are primarily adsorbed and co-precipitated with iron corrosion products.  
13   One may wonder how the  $Fe^0$  technology will develop with the new concept.

14   **Keywords:** Adsorption, Co-precipitation, Contaminant, Removal, Zerovalent iron.

## 15   **Introduction**

16   In 1990 Canadian hydrogeologists have rediscovered iron corrosion as metallic iron ( $Fe^0$ )  
17   became a remediation agent for contaminated aquifers, soils and waters. It was fortuitously  
18   found that  $Fe^0$  eliminated trichloroethylene from aqueous solutions (1-3). Since then intensive  
19   efforts have been devoted to remediation with  $Fe^0$  materials. As result  $Fe^0$  is now regarded as  
20   a very competent reactive agent for remediation of systems that are contaminated with  
21   reducible substances (including chlorinated hydrocarbons, nitrate, nitro aromatics, chromium,  
22   uranium) (4-8).

23   The rediscovery of iron corrosion was followed by a seminal work on the mechanism of  
24   aqueous contaminant removal in the presence of  $Fe^0$  (e.g. in  $Fe^0/H_2O$  systems) (9). These  
25   authors proposed three possible mechanisms for contaminant removal: (i) contaminant  
26   adsorption onto the surface of in situ formed corrosion products, (ii) contaminant reduction by

27  $\text{Fe}^0$  (direct reduction), (iii) contaminant reduction by  $\text{Fe}^{\text{II}}$  or  $\text{H}_2/\text{H}$  (indirect reduction). The  
28 work of Matheson and Tratnyek (9) was re-evaluated by Weber (10) and the results indicate  
29 that (i) direct reduction (electrons from  $\text{Fe}^0$ ) is the major reaction pathway, and (ii) reductive  
30 transformation by  $\text{Fe}^0$  is a surface-mediated process. Accordingly, the involved contaminant  
31 must contact the  $\text{Fe}^0$  surface for electron transfer to take place. Alternatively, the oxide film  
32 on  $\text{Fe}^0$  must be electronic conductive or the system must contain appropriate electron  
33 mediators (so-called “electron shuttles”). Since the work of Weber (10) the know-why of  
34 contaminant removal in  $\text{Fe}^0/\text{H}_2\text{O}$  systems was considered to be achieved and the iron/sand  
35 mixture lost his nickname of “magic sand” (2). However, the acceptance of the concept of  
36 reductive transformation was primarily a consensus (4) as this concept failed to consistently  
37 explained many experimental facts (11-14). For example, while using differential pulse  
38 polarography to investigate the reduction of nitrobenzene in  $\text{Fe}^0/\text{H}_2\text{O}$  systems, Lavine et al.  
39 (11) concluded that their studies were very informative but they couldn't evidence reduction  
40 of organic compounds as mediated by the  $\text{Fe}^0$  surface. Similarly, a very recent work of Jiao et  
41 al. (14) has shown that the reduction of carbon tetrachloride in the presence of  $\text{Fe}^0$  is primarily  
42 mediated by  $\text{H}_2$  from iron corrosion (indirect reduction). Moreover, the quantitative removal  
43 for non-reducible species as methylene blue (15), triazoles (16) and zinc (17) in  $\text{Fe}^0/\text{H}_2\text{O}$   
44 systems has been reported. Because of the inconsistency of the consensus on the mechanism  
45 of contaminant removal in  $\text{Fe}^0/\text{H}_2\text{O}$  systems, it was pertinent to reconsider the  $\text{Fe}^0/\text{H}_2\text{O}$   
46 system as a whole. For this purpose it is necessary to go back to the literature on metal  
47 corrosion.

#### 48 **Fundamental aspects of aqueous metal corrosion**

49 Most metals (M) in their natural state are not pure metals ( $\text{M}^0$ ), but are in the form of metallic  
50 salts (mostly oxides -  $\text{M}_x\text{O}_y$ , sulphides -  $\text{M}_x\text{S}_y$ , and carbonates -  $\text{M}_x(\text{CO}_3)_y$ ). When these metal  
51 ores are refined or smelted, a losing battle with thermodynamics begins with the metal  
52 tending toward formation of metallic oxides, sulphides or carbonates depending on the

53 working environment (18-20). The rate and the extent at which a metal dissolves in an  
54 aqueous environment (immersed metal corrosion) depends on many inter-dependant factors  
55 (18, 21, 22) including: (i) the chemistry of water (pH, salinity, concentration and  
56 concentration of chelating agents), (ii) the nature of the oxide layer formed by initial metal  
57 corrosion (composition, electronic conductivity, porosity and thickness), (iii) the  
58 manufacturing history of the metal (e.g. whether the metal been cast, forged, wrought or  
59 welded), and (iv) the metal thermodynamic susceptibility to oxidation (position on the  
60 reduction-potential scale). It has been established that the most important factor responsible  
61 for immersed metal corrosion under conditions pertinent to natural waters ( $4.5 \leq \text{pH} \leq 9.5$ ) is  
62 the electronic conductivity and the porosity of the oxide layer (23). This statement will be  
63 supported by a classical example.

64 Aluminium ( $E^0 = -1.71 \text{ V}$ ) is more susceptible to oxidation than iron ( $E^0 = -0.44 \text{ V}$ ) but Al is  
65 known to be relatively inert to atmospheric and aqueous corrosion, whereas Fe is very  
66 corrosive. There are two main reasons for this.

67 First, the oxidation of  $\text{Al}^0$  exclusively yields a non-conductive layer of  $\text{Al}_2\text{O}_3$  whereas the  
68 oxidation of  $\text{Fe}^0$  may yield a conductive layer of  $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$  species (e.g.  $\text{Fe}_3\text{O}_4$ , green rust) (24).  
69 Accordingly an oxide film on  $\text{Fe}^0$  may act as a semiconductor and mediate electron transfer  
70 from  $\text{Fe}^0$  (25-27). In this situation  $\text{Fe}^0$  corrosion continues despite the presence of the oxide  
71 film. It is evident, that this behaviour can not be observed under oxic conditions where  $\text{Fe}^{\text{II}}$  is  
72 instable and (at least) the outer layer of the oxide film will exclusively consist of non-  
73 conductive  $\text{Fe}^{\text{III}}$  oxides ( $\text{FeOOH}$  or  $\text{Fe}_2\text{O}_3$ ).

74 Second, the unit-cell in Al and  $\text{Al}_2\text{O}_3$  are very similar to one another; thus the aluminium  
75 oxide can adhere tightly to the metallic aluminium beneath it (23). The oxidized surface  
76 provides a protective layer that prevents oxygen from getting to the underlying Al surface. In  
77 contrast, the packing dimensions of  $\text{Fe}^0$  and Fe oxides are not particularly close; thus there is  
78 no tendency for an iron oxide layer to adhere to metallic iron. Therefore, regarding its

79 protective properties for iron corrosion, the “curse of rust” (23) is not that it forms, but that it  
80 constantly flakes off and exposes fresh iron surface for attack (23, 24). This “curse” of rust  
81 became a “blessing” in using Fe<sup>0</sup> for environmental remediation.

## 82 **Metallic iron for environmental remediation**

83 Fe-based alloys (Fe<sup>0</sup> materials, mostly cast iron and steel) are certainly suitable for  
84 environmental remediation because of their low tendency to passivity due to the porosity and  
85 the instability of generated oxide layers. Instead of this trivial reason, Fe<sup>0</sup> has been considered  
86 as a strong reducing agent for the reductive transformation of several species in natural waters  
87 (3-10). This consideration is not acceptable even from a pure thermodynamic perspective as  
88 the electrode potential of iron is almost the same (about -0.44 V) in low alloyed and stainless  
89 steels (Fe-based alloys). Accordingly, various Fe<sup>0</sup> materials should have exhibited similar  
90 behaviour for the removal of the same species. This has not been the case as for example  
91 Miehr et al. (28) reported variation of rate constants for contaminant removal varying over up  
92 to four orders of magnitude due to differences in Fe<sup>0</sup> “type”.

93 Because Fe<sup>0</sup> materials for environmental remediation are primarily susceptible to oxidation,  
94 complete passivation can only result from the transformation of initially non-protective films  
95 to impervious layers under specific environmental conditions. Therefore, a sake for an  
96 overview of factors likely to influence film formation and transformation (stability and  
97 breakdown) under environmental conditions should be undertaken. This could be a very  
98 difficult task because chemical breakdown occurs when the film is dissolved (e.g. by a  
99 chelating agent) or penetrated chemically (e.g. by a contaminant or Cl ions).

## 100 **Fundamental aspects of contaminant removal in Fe<sup>0</sup>/H<sub>2</sub>O systems**

101 While considering Fe<sup>0</sup> as a reducing agent for contaminant reductive transformation it has  
102 been impossible to explain several experimental and field observations as recalled above (also  
103 see refs. 29 and 30). The main reason for this is that iron corrosion products (oxide film) have  
104 been regarded as simple coatings, mediating at most electron transfer from Fe<sup>0</sup> to the

105 contaminant. However, the oxide film formation and transformation (recrystallization,  
106 dissolution, precipitation) is a dynamic process occurring in the presence of contaminants.  
107 Moreover, the oxide film formation can be regarded as the process of iron precipitation (31-  
108 33). Here, iron precipitation occurs in the presence of small amounts of foreign species  
109 (including contaminants). These foreign species are necessarily sequestered within the oxide  
110 film as discussed in the next section (34). In this manner contaminants are primarily removed  
111 from the aqueous phase by a non-specific mechanism as they are just sequestered in the  
112 matrix of precipitating iron oxides (33). This process is widely used in water treatment by  
113 electrocoagulation using Fe electrodes ( $\text{Fe}^0$  EC) (35, 36) and explains why bacteria, viruses  
114 and thermodynamically non-reducible substances (e.g. Zn) have been quantitatively removed  
115 in  $\text{Fe}^0/\text{H}_2\text{O}$  systems. There are two main differences between passive  $\text{Fe}^0/\text{H}_2\text{O}$  systems and  
116 iron electrocoagulation: (i)  $\text{Fe}^0$  oxidation is electrically accelerated in  $\text{Fe}^0$  EC as the aim is to  
117 quantitatively produce iron hydroxides for contaminant removal by flocculation, and (ii)  
118 while contaminants are flocculated from the bulk solution in  $\text{Fe}^0$  EC, they are precipitated in  
119 the vicinity of  $\text{Fe}^0$  in passive  $\text{Fe}^0/\text{H}_2\text{O}$  systems. Accordingly a passive  $\text{Fe}^0/\text{H}_2\text{O}$  system could  
120 be regarded as a filter (working on the principle of size exclusion) in which species are  
121 additionally trapped by in situ generated iron hydroxides (and oxides).

122 It should be explicitly stated that adsorption, co-precipitation and redox transformations are  
123 not each other exclusive as adsorbed or co-precipitated contaminants may be further (i)  
124 reduced by  $\text{Fe}^0$ , adsorbed or soluble  $\text{Fe}^{\text{II}}$  species or (ii) oxidized by  $\text{HO}^\bullet/\text{H}_2\text{O}_2$  species  
125 (Fenton-like reactions). It is however certain, that the extend of reduction is difficult to  
126 evaluate. This assertion is supported by the fact that to date, no carbon balances between  
127 reactants and supposedly reaction products have ever been successfully done for many  
128 chlorinated hydrocarbons (3). However, one should no care about the fate of co-precipitated  
129 contaminants as they will remain sequestered so far iron oxides are not dissolved.  
130 Alternatively and complementary, the possibility of iron oxide dissolution and its

131 consequence for co-precipitated contaminants should be discussed at each relevant site. The  
132 next section will discuss on the suitability of the  $\text{Fe}^0/\text{H}_2\text{O}$  system for contaminant removal.

### 133 **Peculiarity of the $\text{Fe}^0/\text{H}_2\text{O}$ system**

134 The singularity of the  $\text{Fe}^0/\text{H}_2\text{O}$  system is the in situ generation of soluble  $\text{Fe}^{\text{II}}$  species and their  
135 further transformations to crystalline iron oxides and hydroxides ( $\text{Fe}(\text{OH})_2$ ,  $\text{Fe}(\text{OH})_3$ ,  $\text{Fe}_3\text{O}_4$ ,  
136  $\text{Fe}_2\text{O}_3$ ,  $\text{FeOOH}$ ,  $\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$ ). The various forms of iron oxides, oxyhydroxides, and  
137 hydroxides are called “iron oxides” through the end of this paper. Thus, in an aqueous  
138 solution,  $\text{Fe}^0$  ideally converts to crystalline iron oxides via a sequence of oxidation/  
139 hydrolysis/precipitation/dehydration reactions (Tab. 1). The conversion of  $\text{Fe}^0$  to crystalline  
140 iron oxides goes towards several intermediate stages of amorphous and poorly crystalline  
141 precipitates, including green rust formation and transformation. Intermediate stages also  
142 include solid-state transformation of oxides (recrystallisation). For example, in aqueous  
143 solution crystalline  $\text{Fe}(\text{OH})_2$  may convert to other iron oxides via  
144 oxidation/hydrolysis/dehydration.

145 In essence, iron oxide formation involves two basic mechanisms: (i) direct precipitation from  
146  $\text{Fe}^{2+}/\text{Fe}^{3+}$ -containing solutions, and (ii) transformation of an Fe oxide precursor. Both  
147 mechanisms may occur in natural  $\text{Fe}^0/\text{H}_2\text{O}$  systems, even though direct precipitation is  
148 dominant. Due to the diversity of iron corrosion products (CP), a common problem faced by  
149 studies on  $\text{Fe}^0/\text{H}_2\text{O}$  systems is the proper characterization of available iron oxides (37-39). A  
150 common procedure is the use of synthetic iron oxides to simulate natural CP. However, in  
151 natural  $\text{Fe}^0/\text{H}_2\text{O}$  systems, CP are composed primarily of different iron oxides. Individual iron  
152 oxides possess different chemical properties such as crystal structure, morphology, and  
153 adsorptive properties (Tab. 2). Accordingly, no synthetic iron oxides (or oxide mixtures) can  
154 rigorously simulate natural CP with regard to transformation occurring within.

### 155 **Transformations within $\text{Fe}^0/\text{H}_2\text{O}$ systems**

156 Synthetic iron oxides as simulates for natural iron oxides are prepared in the pure phase while  
157 natural oxides are precipitated and further transformed in the presence of foreign species  
158 (including contaminants). Thus a synthetic oxide can remove contaminant solely by  
159 adsorption while natural oxides incorporate contaminant in their structure while precipitating  
160 (adsorption and co-precipitation). At any moment after implementation of a  $\text{Fe}^0$  reactive wall,  
161 a natural  $\text{Fe}^0/\text{H}_2\text{O}$  system is made up of  $\text{Fe}^0$  and various iron oxides, possibly including  
162 transforming phases like  $\text{FeO}$  which are not stable under natural (sub)surface conditions.  
163 Given that the iron oxides are of various reactivity toward contaminant removal, the  
164 contribution of individual removal mechanisms to decontamination is difficult to access.  
165 However, it is the goal of this paper to demonstrate that, beside adsorption, contaminant  
166 sequestration (co-precipitation) is the sole certain removal mechanism. The occurrence and  
167 the extent of all other processes can be discussed on a contaminant-specific basis. Therefore  
168 adsorption and co-precipitation are the fundamental mechanisms of contaminant removal in  
169  $\text{Fe}^0/\text{H}_2\text{O}$  system. To illustrate the transformations yielding to contaminant sequestration, the  
170 evolution of three iron atoms from the  $\text{Fe}^0$  material will be discussed.

171 The three atoms ( $3 \text{Fe}^0$ ) will be first oxidized to  $3 \text{Fe}^{\text{II}}$  species and may further be oxidized  
172 (e.g. by  $\text{O}_2$ ) to  $3 \text{Fe}^{\text{III}}$  species. Then they will be transformed to colloidal species partly having  
173 specific surface areas (SSA) higher than  $500 \text{ m}^2/\text{g}$  (43, 44) before they aggregate and  
174 crystallize to one  $\text{Fe}_3\text{O}_4$ ,  $1.5 \text{Fe}_2\text{O}_3$  or  $3 \text{Fe}(\text{OH})_2$ ,  $\text{Fe}(\text{OH})_3$  or  $\text{FeOOH}$ . The relative variation  
175 of the volume of resulted crystalline oxides is represented in Fig. 1 using values from Tab. 2.  
176 Fig. 1 clearly shows volume expansion relative to  $3 \text{Fe}^0$  for all iron oxides except magnetite  
177 for which a volume reduction of 30 % was noticed. However, it should be kept in mine that  
178 even magnetite is a final state of a transformation going through even more voluminous  
179 colloidal, amorphous and highly adsorptive species (SSA values in Tab. 2). Although volume  
180 expansion is discussed here on the basis of the volume of crystallized iron oxides, this process  
181 is a rule in the process iron corrosion, irrespective from the nature and the crystallinity of the

182 final products. Thus iron oxidative dissolution and iron oxide precipitation should be regarded  
183 a cycle of volume expansion/contraction in the course of which available contaminants are  
184 adsorbed and sequestered. Sequestered contaminants could be further transformed (oxidized  
185 or reduced).

## 186 **Conclusions**

187 This paper has contributed to open a new avenue for the scientific understanding of processes  
188 of contaminant removal in  $\text{Fe}^0/\text{H}_2\text{O}$  systems. Researchers and practitioners have long  
189 recognized the limits of the reductive transformation concept (11-14). However, the view that  
190 contaminants are primarily adsorbed and co-precipitated with iron corrosion products (29, 30,  
191 33) has partly faced with very sceptic views (45, 46) or is just degraded to an “alternative  
192 hypothesis to be considered” (47). Fortunately, sceptic views are based on the large  
193 acceptability of the concept of reductive transformation which was a consensus (4) and not of  
194 hard experimental facts. While former attempts to disprove the reductive transformation  
195 concept were based on extensive literature review (29, 30) and a munitions examination of the  
196 abundance of reactive species in  $\text{Fe}^0/\text{H}_2\text{O}$  systems (33), the present study is based on a simple  
197 analysis of processes occurring in a  $\text{Fe}^0/\text{H}_2\text{O}$  system. The major output is that  $\text{Fe}^0$  oxidative  
198 dissolution and iron oxide precipitation should be regarded as a cycle of volume  
199 expansion/contraction in the course of which chemical contaminants and pathogens are  
200 adsorbed and sequestered. Because this argument does not care about the nature of a  
201 contaminant, it should be definitively clear that specific interactions are an exception and not  
202 the rule in a  $\text{Fe}^0/\text{H}_2\text{O}$  system (statement 1). Statement 1 is the cornerstone on which  
203 comprehensive knowledge on the behaviour of  $\text{Fe}^0/\text{H}_2\text{O}$  systems under natural conditions  
204 should be acquired. In this effort, it is almost impossible to transfer good results from the  
205 open aqueous iron corrosion. For example, corrosion inhibition of mild steel by methylene  
206 blue (MB) has been reported (48). However, corrosion inhibition is effective with 5.0 mM  
207 (1595 mg/L) MB in HCl at temperatures varying from 30 to 60 °C. The used temperatures are



208 not relevant for groundwater remediation and the needed concentration (1595 mg/L) is even  
209 non relevant for wastewater situations. Additionally the reaction took place in a strong acidic  
210 solution (2 M HCl).

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## 213 **References**

- 214 1. Reynolds, G.W., Hoff, J.T., Gillham, R.W. (1990). Sampling bias caused by materials  
215 used to monitor halocarbons in groundwater. *Environ. Sci. Technol.*, 24, 135-142.
- 216 2. Tratnyek, P.G. (1996). Putting corrosion to use: remediating contaminated groundwater  
217 with zero-valent metals. *Chemistry & Industry* 1 July 1996, 499-503.
- 218 3. Lee, G., Rho, S., Jahng, D. (2004). Design considerations for groundwater remediation  
219 using reduced metals. *Korean J. Chem. Eng.*, 21, 621-628.
- 220 4. O'Hannesin, S.F., Gillham, R.W. (1998). Long-term performance of an in situ "iron wall"  
221 for remediation of VOCs. *Ground Water*, 36, 164-170.
- 222 5. Jambor, J.L., Raudsepp, M., Mountjoy, K. (2005). Mineralogy of permeable reactive  
223 barriers for the attenuation of subsurface contaminants. *Can. Miner.*, 43, 2117-2140.
- 224 6. Henderson, A.D., Demond, A.H. (2007). Long-term performance of zero-valent iron  
225 permeable reactive barriers: a critical review. *Environ. Eng. Sci.*, 24, 401-423.
- 226 7. Cundy, A.B., Hopkinson, L., Whitby, R.L.D. (2008). Use of iron-based technologies in  
227 contaminated land and groundwater remediation: A review. *Sci. Tot. Environ.*, 400, 42-  
228 51.
- 229 8. Thiruvengkatachari, R., Vigneswaran, S., Naidu, R. (2008). Permeable reactive barrier for  
230 groundwater remediation. *J. Ind. Eng. Chem.*, 14, 145-156.
- 231 9. Matheson, L.J., Tratnyek, P.G. (1994). Reductive dehalogenation of chlorinated methanes  
232 by iron metal, *Environ. Sci. Technol.*, 28, 2045-2053.

- 233 10. Weber, E.J. (1996). Iron-mediated reductive transformations: investigation of reaction  
234 mechanism. *Environ. Sci. Technol.*, 30, 716-719.
- 235 11. Lavine, B.K., Auslander, G., Ritter, J. (2001). Polarographic studies of zero valent iron as  
236 a reductant for remediation of nitroaromatics in the environment. *Microchem. J.*, 70, 69-  
237 83.
- 238 12. Mantha, R., Taylor, K.E., Biswas, N., Bewtra, J.K. (2001). A continuous system for Fe<sup>0</sup>  
239 reduction of nitrobenzene in synthetic wastewater. *Environ. Sci. Technol.*, 35, 3231-3236.
- 240 13. Mielczarski, J.A., Atenas, G.M., Mielczarski, E. (2005). Role of iron surface oxidation  
241 layers in decomposition of azo-dye water pollutants in weak acidic solutions. *Appl. Catal.*  
242 *B: Environ.*, 56, 289-303.
- 243 14. Jiao, Y., Qiu, C., Huang, L., Wu, K., Ma, H., Chen, S., Ma, L., Wu, L. (2009). Reductive  
244 dechlorination of carbon tetrachloride by zero-valent iron and related iron corrosion. *Appl.*  
245 *Catal. B: Environ.*, 91, 434-440.
- 246 15. Noubactep, C. (2009). Characterizing the discoloration of methylene blue in Fe<sup>0</sup>/H<sub>2</sub>O  
247 systems. *J. Hazard. Mater.* 166, 79-87.
- 248 16. Jia, Y., Aagaard, P., Breedveld, G.D. (2007). Sorption of triazoles to soil and iron  
249 minerals. *Chemosphere*, 67, 250-258.
- 250 17. Morrison, S.J., Metzler, D.R., Dwyer, B.P. (2002). Removal of As, Mn, Mo, Se, U, V and  
251 Zn from groundwater by zero-valent iron in a passive treatment cell: reaction progress  
252 modelling. *J. Cont. Hydrol.*, 56,99-116.
- 253 18. Van Orden, A.C. (1989). Corrosion mechanisms relevant to high-level waste repositories.  
254 *Eng. Geol.*, 26, 331-349.
- 255 19. Brondel, D., Edwards, R., Hayman, A., Hill, D., Mehta, S., Semerad, T. (1994). Corrosion  
256 in the oil industry. *Oilfield Rev.*, 6, 4-18.
- 257 20. Schmuki, P. (2002). From Bacon to barriers: a review on the passivity of metals and  
258 alloys. *J. Solid State Electrochem.*, 6, 145-164.

- 259 21. Wilson, E.R. (1923). The mechanism of the corrosion of iron and steel in natural waters  
260 and the calculation of specific rates of corrosion. *Ind. Eng. Chem.*, 15, 2 127-133.
- 261 22. Whitman, G.W., Russel, R.P., Altieri, V.J. (1924). Effect of hydrogen-ion concentration  
262 on the submerged corrosion of steel. *Ind. Eng. Chem.*, 16, 665-670.
- 263 23. Dickerson, R.E., Gray, H.B., Haight, Jr., G.P. (1979). *Chemical Principles*, 3rd edition.  
264 Benjamin/Cummings Inc. London, Amsterdam.
- 265 24. Müller, W.J. (1939). Passivity and corrosion of metals. (in German) *Colloid Polymer Sci.*,  
266 86, 150-166.
- 267 25. Bonin, P.M.L., Odziemkowski, M.S., Gillham, R.W. (1998). Influence of chlorinated  
268 solvents on polarization and corrosion behaviour of iron in borate buffer. *Corros. Sci.*, 40,  
269 1391-1409.
- 270 26. Odziemkowski, M.S., Gui, L., Gillham, R.W., Irish, D.E. (2000). The role of oxide films  
271 in the reduction of N-nitrosodimethylamine with reference to the iron groundwater  
272 remediation technology. In: Hebert, K.R., Lillard, R.S., MacDougall, B.R. (Eds), *Oxide*  
273 *Films, Proc. Internat. Symp. The Electrochemical Society, Inc., Pennington, NJ. Vol.*  
274 *2000-4, 357368.*
- 275 27. Scherer, M.M., Richter, S., Valentine, R.L., Alvarez, P.J.J. (2000). Chemistry and  
276 microbiology of permeable reactive barriers for in situ groundwater clean up. *Rev.*  
277 *Environ. Sci. Technol.*, 30, 363-411.
- 278 28. Miehr, R., Tratnyek, G.P., Bandstra, Z.J., Scherer, M.M., Alowitz, J.M., Bylaska, J.E.  
279 (2004). Diversity of contaminant reduction reactions by zerovalent iron: Role of the  
280 reductate. *Environ. Sci. Technol.* 38, 139-147.
- 281 29. Noubactep, C. (2007). Processes of contaminant removal in "Fe<sup>0</sup>-H<sub>2</sub>O" systems revisited:  
282 The importance of co-precipitation. *Open Environ. J.*, 1, 9-13.
- 283 30. Noubactep, C. (2008). A critical review on the mechanism of contaminant removal in  
284 Fe<sup>0</sup>-H<sub>2</sub>O systems. *Environ. Technol.*, 29, 909-920.

- 285 31. Sikora, E., Macdonald, D.D. (2000). The Passivity of Iron in the Presence of  
286 Ethylenediaminetetraacetic Acid I. General Electrochemical Behavior. *J. Electrochem.*  
287 *Soc.*, 147, 4087-4092.
- 288 32. Nesic, S. (2007). Key issues related to modelling of internal corrosion of oil and gas  
289 pipelines – A review. *Corros. Sci.*, 49, 4308-4338.
- 290 33. Noubactep, C. (2009). An analysis of the evolution of reactive species in Fe<sup>0</sup>/H<sub>2</sub>O  
291 systems. *J. Hazard. Mater.*, 168, 1626-1631.
- 292 34. Crawford, R.J., Harding, I.H., Mainwaring, D.E. (1993). Adsorption and coprecipitation  
293 of single heavy metal ions onto the hydrated oxides of iron and chromium. *Langmuir*, 9,  
294 3050-3056.
- 295 35. Mollah, M.Y.A., Schennach, R., Parga, J.R., Cocke, D.L. (2001). Electrocoagulation (EC)  
296 – science and applications. *J. Hazard. Mater.*, 84, 29-41.
- 297 36. Moreno, C.H.A., Cocke, D.L., Gomes, J.A.G., Morkovsky, P., Parga, J.R., Peterson, E.,  
298 Garcia, C. (2009). Electrochemical reactions for electrocoagulation using iron electrodes.  
299 *Ind. Eng. Chem. Res.*, 48, 2275-2282.
- 300 37. Mackenzie P.D., Horney D.P., Sivavec T.M. (1999). Mineral precipitation and porosity  
301 losses in granular iron columns. *J. Hazard. Mater.* 68, 1-17.
- 302 38. Roh Y., Lee S.Y., Elless M.P. (2000). Characterization of corrosion products in the  
303 permeable reactive barriers. *Environ. Geol.*, 40, 184-194.
- 304 39. Borch, T., Camper, A.K., Biederman, J.A., Butterfield, P.W., Gerlach, R., Amonette, J.E.  
305 (2008). Evaluation of characterization techniques for iron pipe corrosion products and iron  
306 oxide thin films. *J. Environ. Eng.*, 134, 835-844.
- 307 40. Borggaard, O.K. (1991). Effects of phosphate on iron oxide dissolution in  
308 ethylenediamine-N,N,N',N'-tetraacetic acid and oxalate. *Clays Clay Miner.*, 39, 324-328.
- 309 41. Balasubramaniam, R., Ramesh, K.A.V., Dillmann, P. (2003). Characterization of rust on  
310 ancient Indian iron. *Curr. Sci.*, 85, 1546-1555.

- 311 42. Caré, S., Nguyen, Q.T., L'Hostis, V., Berthaud, Y. (2008). Mechanical properties of the  
312 rust layer induced by impressed current method in reinforced mortar. *Cement Concrete*  
313 *Res.*, 38, 1079-1091.
- 314 43. Cornell R.M., Schwertmann U. (1996). *The iron oxides*. Wiley-VCH, 573 pp.
- 315 44. Subrt, J., Bohacek, J., Stengl, V., Grygar, T., Bezdicøka, P. (1999). Uniform particles with  
316 a large surface area formed by hydrolysis of  $\text{Fe}_2(\text{SO}_4)_3$  with urea. *Mater. Res. Bull.*, 34,  
317 905-914.
- 318 45. Elsner, M., Cwiertny, D.M., Roberts, A.L., Lollar, B.S. (2007). Response to Comment on  
319 “1,1,2,2-Tetrachloroethane Reactions with  $\text{OH}^-$ , Cr(II), Granular Iron, and a Copper-Iron  
320 Bimetal: Insights from Product Formation and Associated Carbon Isotope Fractionation”.  
321 *Environ. Sci. Technol.*, 41, 7949-7950.
- 322 46. Kang, S.-H., Choi, W. (2009). Response to Comment on “Oxidative Degradation of  
323 Organic Compounds Using Zero-Valent Iron in the Presence of Natural Organic Matter  
324 Serving as an Electron Shuttle”. *Environ. Sci. Technol.*, 43, 3966-3967.
- 325 47. Gui, L., Jeen, S-W., Blowes, D.W., Gillham, R.W., Yang, Y., Reply to the Comment on  
326 “Reduction of Chromate by Granular Iron in the Presence of Dissolved  $\text{CaCO}_3$  ” by C.  
327 Noubactep, *Appl. Geochem.* (2009), doi: 10.1016/j.apgeochem.2009.08.006.
- 328 48. Oguzie, E.E. (2005). Corrosion inhibition of mild steel in hydrochloric acid solution by  
329 methylene blue dye. *Mater. Lett.*, 59, 1076-1079.
- 330

330 **Table 1:** Relevant reactions for the process of aqueous Fe<sup>0</sup> dissolution, iron corrosion  
 331 products formation and contaminant (Ox) removal in Fe<sup>0</sup>/H<sub>2</sub>O system. Red is a  
 332 reduced form of Ox. FeOOH is a proxy of corrosion products and Fe<sub>x</sub>(OH)<sub>y</sub><sup>(3x-y)</sup> is  
 333 an iron hydroxide.

Process	Reaction	Eq.
<b>Fe<sup>0</sup> dissolution</b>	$\text{Fe}^0 \Leftrightarrow \text{Fe}^{2+} + 2 \text{e}^-$	1
<b>Fe<sup>0</sup> passivation</b>	$\text{Fe}^0 + \text{H}_2\text{O} \Rightarrow \text{Fe}(\text{O})_{\text{ads}} + 2 \text{H}^+ + 2\text{e}^-$	2
<b>Fe<sup>0</sup> depassivation</b>	$\text{Fe}(\text{O})_{\text{ads}} + 2\text{H}^+ \Rightarrow \text{Fe}^{2+} + \text{H}_2\text{O}$	3
	$\text{Fe}(\text{O})_{\text{ads}} + \text{H}_2\text{O} \Rightarrow \text{Fe}(\text{OH})_2$	4
	$\text{Fe}(\text{O})_{\text{ads}} + \text{OH}^- \Rightarrow \text{HFeO}_2^-$	5
<b>H<sub>2</sub> evolution</b>	$2 \text{H}^+ + 2\text{e}^- \Rightarrow \text{H}_2\uparrow$	6
<b>O<sub>2</sub> reduction</b>	$\text{O}_2 + 2 \text{H}_2\text{O} + 4 \text{e}^- \Rightarrow 4 \text{OH}^-$	7
<b>Fe<sup>2+</sup> oxidation</b>	$\text{Fe}^{2+} \Rightarrow \text{Fe}^{3+} + \text{e}^-$	8
	$\text{Fe}^{2+} + 2 \text{OH}^- \Rightarrow \text{Fe}(\text{OH})_2$	9
	$\text{Fe}^{3+} + 3 \text{OH}^- \Rightarrow \text{Fe}(\text{OH})_3$	10
<b>Scale formation</b>	$\text{Fe}(\text{OH})_2 \Rightarrow \text{FeO} + \text{H}_2\text{O}$	11
	$2 \text{Fe}(\text{OH})_3 \Rightarrow \text{Fe}_2\text{O}_3 + 3 \text{H}_2\text{O}$	12
	$4 \text{Fe}(\text{OH})_3 \Rightarrow \text{Fe}(\text{OH})_2 + \text{Fe}_3\text{O}_4 + 5 \text{H}_2\text{O} + \frac{1}{2} \text{O}_2$	13
	$\text{Fe}(\text{OH})_3 \Rightarrow \text{FeOOH} + \text{H}_2\text{O}$	14
<b>Ox reduction</b>	$\text{Fe}^0 + \text{Ox}_{(\text{aq})} \Rightarrow \text{Fe}^{2+} + \text{Red}_{(\text{s or aq})}$	15
	$\text{Fe}^{\text{II}}_{(\text{aq})} + \text{Ox}_{(\text{aq})} \Rightarrow \text{Fe}^{\text{III}} + \text{Red}_{(\text{s or aq})}$	16
	$\text{Fe}^{\text{II}}_{(\text{s})} + \text{Ox}_{(\text{aq or aq})} \Rightarrow \text{Fe}^{\text{III}} + \text{Red}_{(\text{s or aq})}$	17
	$\text{H}_2 + \text{Ox}_{(\text{aq or aq})} \Rightarrow \text{H}^+ + \text{Red}_{(\text{s or aq})}$	18
<b>Ox adsorption</b>	$\text{FeOOH} + \text{Ox}_{(\text{aq})} \Leftrightarrow \text{FeOOH-Ox}$	19
<b>Ox co-precipitation</b>	$\text{Ox}_{(\text{aq})} + n \text{Fe}_x(\text{OH})_y^{(3x-y)} \Leftrightarrow \text{Ox}[\text{Fe}_x(\text{OH})_y^{(3x-y)}]_n$	20

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335

335 **Table 2:** Some relevant characteristics of metallic iron and its main corrosion products. SSA  
 336 is the specific surface area.  $V_{\text{rust}}/V_{\text{Fe}}$  is theoretical ratio between the volume of  
 337 expansive corrosion products and the volume of iron in the  $\text{Fe}^0$  material. Data from  
 338 refs. 40-42.

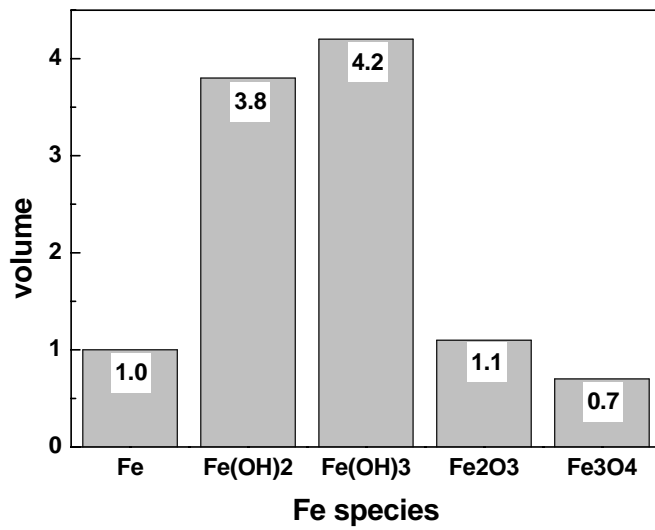
Species	Formula	Symmetry	Density	SSA ( $\text{m}^2/\text{g}$ )	$V_{\text{rust}}/V_{\text{Fe}}$
Iron	Fe	bcc	7.86	<1	-
Magnetite	$\text{Fe}_3\text{O}_4$	Cubic	5.18	6.0	2.08
Hematite	$\alpha\text{-Fe}_2\text{O}_3$	Rhombohedral	5.26	64	2.12
Maghemite	$\gamma\text{-Fe}_2\text{O}_3$	Cubic	4.69	30	n.a.
Goethite	$\alpha\text{-FeOOH}$	Orthorhombic	4.28	82	2.91
Akageneite	$\beta\text{-FeOOH}$	Tetragonal	3.55	41	3.48
Lepidocrocite	$\gamma\text{-FeOOH}$	Orthorhombic	4.09	221	3.03
	$\text{Fe}(\text{OH})_2$	Trigonal	3.4	n.a.	3.75
Bernalite	$\text{Fe}(\text{OH})_3$	Orthorhombic	3.35	328	4.2

339 n.a. = not available.

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343 **Figure 1:** Relative volumes of iron and selected crystalline corrosion reaction products. The  
344 values is the bar represent the expansion coefficient. The calculations were made  
345 for three iron atoms and show that a volume compression will occur upon  
346 formation of Fe<sub>3</sub>O<sub>4</sub>. Strictly any crystallization goes through dissolution,  
347 nucleation and aggregation. Intermediate species are of high specific area and even  
348 more voluminous than crystalline Fe(OH)<sub>3</sub>.