

1 **Fe⁰-based alloys for Environmental Remediation: Thinking outside the Box**

2 Noubactep C.^{*(a)}, Schöner A.^(b)

3 ^(a) Angewandte Geologie, Universität Göttingen, Goldschmidtstraße 3, D - 37077 Göttingen, Germany.

4 ^(b) Institut für Geowissenschaften, Ingenieurgeologie, Martin-Luther-Universität Halle; Von-Seckendorff-Platz 3,
5 D - 06120 Halle, Germany.

6

7 (*) corresponding author: cnoubac@gwdg.de;

8 Tel. +49 551 39 3191, Fax: +49 551 399379

9

10 **Abstract**

11 A review of the approach used by environmental remediation researchers to evaluate the
12 reactivity of Fe⁰-based alloys reveals the lack of consideration of the results available from
13 other branches of science. This paper discusses the limitations of the current approach. The
14 discussion provided here suggests that the current assumption that redox-sensitive species
15 serve as corrosive agents for Fe⁰ maybe incorrect because water as the solvent is also
16 corrosive. A new approach is proposed in which water is considered as the primary Fe⁰
17 oxidizing agent and the impact of individual relevant solutes (including contaminants) should
18 be assessed in long-term laboratory experiments. It is expected that the application of the
19 proposed approach will help to reliably characterize the reactivity of Fe⁰ materials within a
20 few years.

21 **Keywords:** Adsorption, Co-precipitation, Groundwater, Remediation, Zerovalent Iron.

22 **Capsule:** Current controversies on Fe⁰/H₂O systems result from misinterpretation of Fe⁰
23 corrosion.

24 **Introduction**

25 Iron permeable reactive barriers (iron walls) are a valuable technological application that has
26 been shown to be both environmentally friendly and cost-effective in the removal of various
27 substances from contaminated waters [1-3]. Since its development in 1990, by Canadian

28 hydrogeologist, numerous papers have been written on the topic and approximately 120 iron
29 walls installed worldwide [1-4]. Laboratory tests have demonstrated that other metals (e.g.,
30 Zn, Mg, Sn) are also effective in removing contaminants from water. The advantage of iron
31 over other metals is that they are non-toxic (environmentally friendly), inexpensive and
32 readily available in bulk quantities (cost-effective). Fe⁰-based alloys commonly referred to as
33 “zero valent iron”, “elemental iron”, “iron fillings” or “granular iron”, are commercially
34 available and produced from scrap iron and steel [2, 3].

35 Since the introduction of the iron wall technology, reductive transformations of compounds
36 (degradation of organics and precipitation of inorganics) by Fe⁰ mostly under anoxic
37 conditions has been extensively investigated [1,2,3]. In the recent years, oxidative
38 transformations of compounds by Fe⁰ has been also investigated [5-11]. During the oxidation
39 of Fe⁰ under oxic conditions, both ferrous iron and superoxide radicals are generated, leading
40 to the production of strong oxidants that are able to degrade various contaminants. Therefore,
41 oxidative transformations by Fe⁰ should be regarded as Fenton-like processes [6,10]. The
42 aqueous oxidation of Fe⁰ leads to the formation of reactive intermediates both under oxic
43 (Fe^{II}, H₂O₂, OH[•]) and anoxic (Fe^{II}, H₂/H) conditions. Fe^{II} species are subsequently (at least
44 partly) oxidized to Fe^{III} and form hydrous Fe^{II}/Fe^{III} oxides with larger adsorption capacities
45 than the Fe⁰ surface, such that there is a potential for (oxidative or/and reductive)
46 transformation and removal of a range of inorganic and organic contaminants [10,12]. The
47 subsequent presentation will be mainly focused on the reductive pathway as it is the one more
48 likely to occur in the subsurface.

49 Despite two decades of intensive research, the mechanism of reductive contaminant removal
50 by Fe⁰ in reactive walls is not completely understood. The current conceptual model for
51 reductive transformations assumes that Fe⁰-based alloys mostly reduce (Eq. 1) and/or adsorb
52 (Eq. 2) contaminants (Ox). This concept persists in current literature despite a number of
53 papers that have attempted to point out the limits of the concept [13-20]. Noubactep [12,18]

54 has demonstrated that adsorption (Eq. 2) and co-precipitation (Eq. 3) are the fundamental
55 mechanisms of contaminant removal from the aqueous phase by Fe^0 -based alloys (e.g., in
56 $\text{Fe}^0/\text{H}_2\text{O}$ systems). A subsequent abiotic reduction may be driven by four different reaction
57 paths (Table 1), the reaction path chosen depends on the origin of electrons and the nature of
58 the contaminant: (i) reduction by Fe^0 (direct reduction), (ii) reduction by aqueous Fe^{II} ($\text{Fe}^{\text{II}}_{(\text{aq})}$)
59 - Eq. 4), (iii) reduction by adsorbed or structural Fe^{II} ($\text{Fe}^{\text{II}}_{(\text{s})}$ - Eq. 5), and (iv) reduction by
60 molecular (H_2) or atomic (H) hydrogen (Eq. 6).

61 The current concept considers direct reduction (Eq. 1) as the primary removal mechanism for
62 redox-sensitive contaminants. This assumption is somewhat arbitrary as it can not explain
63 why redox-insensitive contaminants and living organisms are quantitatively removed in
64 $\text{Fe}^0/\text{H}_2\text{O}$ systems [12]. The present communication suggests that direct reduction as the
65 primary removal mechanism in the neutral pH range is in conflict with current conceptual
66 model for iron corrosion and experimental results on iron corrosion produced in the petroleum
67 and hydrometallurgy industries. Therefore, one of the major problems in implementation of
68 the iron wall technology is the improper consideration of the large volume of literature
69 available on iron corrosion. In this article several suggestions are provided that will contribute
70 to the development of this innovative and efficient technology for the remediation of soils and
71 groundwater; in particular, the impact of individual contaminants on the mechanisms of iron
72 corrosion under site specific conditions. In other words, the impact of various contaminants
73 on the formation of the oxide-film as well as any changes in the protective properties of this
74 layer under relevant environmental and geochemical conditions will affect the deployment of
75 this technology.

76 **Aqueous Iron Corrosion**

77 Iron exists in nature as stable carbonates, oxides or sulphides. The refining process that
78 produces iron and steel (Fe^0) requires energy. Corrosion is nature's way of reversing an
79 unnatural process back to a lower energy state. Unlike aluminium [$\text{Al}^{\text{III}}/\text{Al}^0$ ($E^\circ = -1.71 \text{ V}$) –

80 Al^0 is more susceptible to oxidation than Fe^0 ; $\text{Fe}^{\text{II}}/\text{Fe}^0$ ($E^0 = -0.44 \text{ V}$) which does not “rust
81 away” on exposure to aqueous environment, Fe^0 -based alloys are readily transformed to
82 natural hydroxides and oxides [$\text{Fe}(\text{OH})_2$, $\text{Fe}(\text{OH})_3$, FeO , FeOOH , Fe_2O_3 , Fe_3O_4]. The
83 generated film of mixed oxides (oxide-film) on Fe^0 is known to be non-protective because it
84 is non-adhesive and porous, and thus permeable to the aggressive aqueous solution.
85 Therefore, it is not only the relative low electrode potential of the couple $\text{Fe}^{\text{II}}/\text{Fe}^0$ ($E^0 = -0.44$
86 V), it is the non-adhesive property of iron corrosion products that determines the suitability of
87 Fe^0 -based alloys for environmental remediation [21, 22]. Since generated oxide-film constantly
88 flakes off and exposes a fresh Fe^0 surface, corrosion will ideally continue until Fe^0 is
89 depleted.

90 Fe^0 is primarily oxidized to Fe^{II} species which are released into the aqueous solution. Two
91 electrons are left behind and migrate to a region where they reduce oxygenated water
92 (yielding aqueous OH^-) or reduce protons to produce molecular hydrogen (H_2). The fate of
93 Fe^{II} from Fe^0 oxidation depends on the solution chemistry. In the presence of dissolved O_2
94 (and related oxidants, e.g., MnO_2), Fe^{II} will be oxidized to insoluble Fe^{III} species. The
95 oxidation of Fe^{II} to Fe^{III} allows ferric iron to be removed from solution as ferric hydroxide or
96 oxyhydroxides (Fig. 1). During this precipitation process the available foreign species
97 (including contaminants) may be entrapped in the iron oxide matrix. Therefore, in addition to
98 the processes of adsorption and reduction, co-precipitation (Table 1), a well documented
99 unspecified contaminant removal mechanism, is another mechanism that must be considered
100 when discussing the processes involved in contaminant removal [12, 18, 23-28].

101 The mechanism of contaminant co-precipitation in $\text{Fe}^0/\text{H}_2\text{O}$ systems can be given as follows:
102 Fe^{II} from Fe^0 oxidation is further oxidized to Fe^{III} . The solubility of Fe^{III} compounds is
103 sufficiently small to form precipitates (Fig. 1). Figure 1 illustrates the pH dependence of Fe^{III}
104 solubility. The next section discusses the spontaneous precipitation of iron from an over-
105 saturated solution in some details. The most common species of Fe^{III} in natural waters is

106 hydrated Fe^{III} hydroxide oxide, which is commonly positively charged [28]. The Fe^{III}
107 precipitates electrostatically co-precipitate negatively charged colloids and dissolved
108 substances, including organic matter [29]. According to Gu et al. [29], ligand exchange is the
109 main binding mechanism between hematite ($\alpha\text{-Fe}_2\text{O}_3$) and dissolved organic matter.

110 The corrosion of Fe^0 in neutral aqueous media is intimately connected with the properties of
111 their surface oxide-film [30, 31]. The corrosive property of water on steel is determined by its
112 chloride and sulphate contents [32, 33]. According to Vetter [30], metals generally corrode by
113 processes that occur at, in, or through a surface oxide-film. The mechanism of action of a
114 given solute (e.g., anion such as chloride) on iron corrosion in near neutral solution involves
115 the following steps: (i) reduction of the dissolution rate of the oxide-film, (ii) repair of the
116 oxide-film by promotion of the reformation of oxide, (iii) repair of the oxide-film by plugging
117 pores and coating the surface with insoluble compounds, (iv) prevention of the adsorption of
118 aggressive anions.

119 In other words, iron is corroded by water (solvent) and the extent of corrosion is more or less
120 influenced by the presence of certain solutes. An alternative approach to investigate the
121 removal process of a given contaminant in the $\text{Fe}^0/\text{H}_2\text{O}$ system is to characterize its impact on
122 the oxide-film under site specific conditions (contaminant concentration, pH, water velocity).

123 This type of research must be conducted with a control system (i.e., a system that is devoid of
124 the contaminant). Also in this research, a system that uses high contaminant concentrations to
125 mimic long-term, low contaminant fluxes should be avoided or only used for qualitative
126 purposes.

127 **The process of spontaneous iron precipitation**

128 Since this paper deals with (hydr)oxide layer formation on Fe^0 surface and its role in aqueous
129 contaminant removal, the process of spontaneous iron precipitation from over-saturated
130 solutions is considered here in some details on a thermodynamic perspective. In the course of
131 spontaneous iron oxide precipitation from electrolyte solutions the dissolved iron

132 concentration lowers. Ideally, at any time, an equilibrium exists between the dissolved Fe
133 species and the precipitates formed earlier (at higher concentrations). Figure 1 compares the
134 solubility of Fe^{III} (data from Liu and Millero [34]) and the line corresponding to 150 µg/L.
135 The arbitrarily selected iron concentration of 150 µg/L (or 27 µmol l⁻¹) corresponds to 1 %
136 Fe⁰ consumption in an experiment using 0.15 g Fe⁰/L [10]. This iron concentration (27 µmol
137 l⁻¹) is by far lower than currently used initial contaminant concentrations. On the other side
138 acid wash as material pre-treatment operation was shown to consume up to 15 % initial Fe⁰
139 amount [4]. Therefore, the selected iron concentration is by far lower than concentrations
140 expected in laboratory batch experiments. It can be seen from figure 1 that when only 1% of
141 the used Fe⁰ reacts an over-saturated Fe solution is obtained at all initial pH values > 3.5.
142 More intensive Fe⁰ consumption inevitably yields higher pH values. Therefore, unless a
143 buffer (or a complexing agent) is used, contaminant removal experiments by Fe⁰ are mostly
144 conducted under conditions where spontaneous iron precipitation is favourable. Even when a
145 buffer is used, iron oxide precipitation at constant pH will be accompanied by contaminant
146 co-precipitation. It is certain that contaminant co-precipitation will be more favourable at pH
147 values where adsorptive interactions with iron oxides are larger (higher pH values) and will
148 depend on the nature of iron oxides (adsorption capacity, crystallinity, point of zero charge,
149 porosity, surface area) [35]. However, unspecific contaminant co-precipitation (simple
150 entrapment) will occur whenever iron oxide precipitate [24,25]. In this regard, it is very
151 important to notice recent results of Gyliene et al. [11] on EDTA co-precipitation in Fe⁰/H₂O
152 systems. Attesting that even the presence of chelating agent will only delay contaminant co-
153 precipitation.

154 **Corrosion in the Petroleum Industry**

155 Corrosion resistant steel is an important class of material used in manufacturing pipe
156 materials for the petroleum industry. Petroleum is formed by various liquid and gaseous
157 hydrocarbons which are extracted in numerous products: lubricant oil, gasoline, diesel,

158 kerosene, and various other products that are used as raw material in the petrochemical
159 industry. Petroleum also contains many impurities: oxygen, nitrogen, sulfur, water, heavy
160 metals, chloride, mineral salt, and sand [36-38].

161 It is well known, that petroleum hydrocarbons (e.g., grease) protect Fe^0 surfaces (including
162 stainless steel) against corrosion. Accordingly, a way of protecting Fe^0 against corrosion is to
163 apply oil on their surface [36]. But crude oil is corrosive due to the presence of the above-
164 mentioned impurities. There are four primary corrosive substances in the production of oil
165 and gas: carbon dioxide, dissolved oxygen, hydrogen sulfide, and water [37-39].

166 It is essential to note that H_2O is corrosive to Fe^0 -based alloys (mostly stainless steel) used in
167 the petroleum industry. Therefore, it is rather surprising that, while using Fe^0 (cast iron and
168 low alloy steels) in a situation where H_2O is the solvent (groundwater and wastewater
169 remediation) it has been assumed that redox-sensitive solutes will drive Fe^0 oxidation.
170 Though other solutes may be thermodynamically more reactive than H_2O , the stoichiometric
171 abundance of water is an argument for quantitative Fe^0 oxidation by the solvent. Another
172 important fact from the petroleum industry that is relevant for investigations into the process
173 of contaminant removal in $\text{Fe}^0/\text{H}_2\text{O}$ systems is the acceleration of the electrochemical Fe^0
174 oxidation through mechanical factors (erosion–corrosion).

175 When a metal is exposed to a flowing corrosive environment erosion–corrosion may occur.
176 When erosion removes the protective film of corrosion products (oxide-film), corrosion may
177 occur at a faster rate. According to Guo et al. [40] the resulted corrosion extent (e.g. mass
178 loss) is often much higher than ordinary summation of the mass loss due to pure erosion and
179 that due to pure corrosion. The additional mass loss is defined by the term of a synergistic
180 effect, which has a substantial contribution to the total metal loss of the components suffering
181 erosion–corrosion. Consequently, experimental designs that have mixing operations capable
182 of inducing erosion–corrosion (too high mixing intensities) should be avoided while
183 investigating processes in $\text{Fe}^0/\text{H}_2\text{O}$ systems that are relevant to natural systems (groundwater).

184 **Fe⁰-based alloys in Hydrometallurgy**

185 The precipitation reaction of a noble metal from its salt solution by a less noble metal is called
186 cementation in hydrometallurgy, and is widely used in industry for the recovery of metals and
187 purification of electrolyte solutions. For example, recovery of dissolved copper with iron as
188 the precipitant metal from leach solutions by the cementation process has been successfully
189 used for several centuries [41, 42]. Due to different standard reduction potentials (Cu^{II}/Cu⁰:
190 +0.34 V; Fe^{II}/Fe⁰: -0.44 V), Cu²⁺ ion becomes readily reduced on Fe⁰ surface, while the
191 corresponding amount of iron is dissolved (Eq. 7).



193 The ratio of iron consumed to produce copper is generally larger than 2 due to various side
194 reactions partly enumerated by Annamalai and Murr [42]. The reaction is performed under
195 acidic conditions (pH ≤ 3). Under such conditions iron is very soluble and the corrosion
196 products that are generated are less adsorptive for dissolved cations (pH < pH_{pzc}).

197 In using cementation in “iron wall technology” factors affecting Fe⁰ reactivity has not been
198 properly addressed or investigated. In particular, at pH values that are relevant to natural
199 systems, iron readily precipitates and the adsorptive affinity of the oxide-film for cations is
200 increased (pH > pH_{pzc}). Therefore, it is surprising that adsorption and co-precipitation has
201 received less attention in the discussion results of cation removal by Fe⁰/H₂O systems [43,
202 44]. Hao et al. [44] reported that Cu²⁺ enhances nitrate reduction by Fe⁰. Even though this is
203 possible through an indirect reaction, “NO₃⁻ removal” and “NO₃⁻ reduction” are not randomly
204 interchangeable without precise investigations. It is more likely that “NO₃⁻ removal” results
205 from co-precipitation with increased corrosion products from Cu²⁺ reduction.

206 Many studies on the removal of reducible metallic ions (including Cr^{VI}) in Fe⁰/H₂O systems
207 demonstrated the feasibility of the application, but did not evaluate the reactions in any depth
208 nor properly exploit the available data from hydrometallurgy. Another important result from
209 hydrometallurgy that has not been properly considered is the importance of surface deposits.

210 When surface deposit effects are neglected, interpretation of cementation rate data, as well as
211 rate data of any heterogeneous reaction involving a solid phase, can often be misleading [41].
212 Accordingly, the significant of oxide film on Fe^0 surface should have been closer
213 investigated.

214 **Concluding Remarks**

215 This paper has attempted to show that the literature on “iron wall technology” has not
216 properly considered data available in three other areas of science that study Fe^0 : (i) aqueous
217 metal corrosion, (ii) corrosion in the petroleum industry, and (iii) hydrometallurgy. In
218 addition to the other areas of science highlighted in this article data from the synthetic organic
219 chemistry have not been carefully considered [45, 46]. For example, Noubactep [46] recalls
220 that aqueous reduction with elemental metals (e.g. Fe^0 , Zn^0 and Sn^0) are quantitative in acidic
221 solutions and mostly at elevated temperatures. Aqueous metal corrosion demonstrates that
222 iron corrosion yields a non-adherent and porous oxide-film that limits the H_2O access or
223 slows down the corrosion process. Consequently, Fe^0 is corroded by H_2O (solvent) and the
224 impact of individual water constituents (including contaminants) should be investigated under
225 site-relevant conditions. Results from the petroleum industry demonstrate that besides H_2O ;
226 H_2S , CO_2 , and molecular O_2 also accelerate corrosion. Moreover, depending on the
227 hydrodynamics erosion-corrosion may also play an important role in groundwater remediation
228 with Fe^0 . Hydrometallurgy demonstrates that Fe^0 is an efficient cementation agent under
229 acidic and stirred conditions. The current literature has not properly utilized these results;
230 knowledge of reaction mechanisms and the factors that influence them appear to be limited. It
231 is almost impossible to make any reliable predictions about the magnitude of removal for any
232 species in a system that has not been investigated. Hopefully, future research in this area will
233 help to eliminate the current knowledge deficiency within a few years. For this purpose, the
234 reactivity of Fe^0 may be first characterised in a contaminant-free system; e.g., dilute EDTA
235 solutions [47, 48]. Once the reactivity (forward dissolution) has been characterised, selected

236 Fe⁰ can be evaluated in long-term experiments designed to evaluate the impact of the
237 variables (E_H or O₂ availability, alkalinity, and NO₃⁻) selected by Henderson and Demond [3]
238 as significant in influencing iron wall performance on the contaminant removal.

239 The authors hope that this article will stimulate or sustain a broader discussion on the process
240 of contaminant removal in Fe⁰/H₂O systems. For this discussion to be effective, expertise that
241 extends beyond one or few research groups is needed. Such an effort may provide the
242 environmental science community with basic information for a non-site-specific iron wall
243 design. Site-specific treatability studies may only be required to fine-tune the design for
244 optimal performance. The proper consideration of available information on Fe⁰ corrosion
245 should accelerate development of the iron wall technology. The first step in this effort is to
246 stop regarding Fe⁰ as major reducing agent in Fe⁰/H₂O systems and properly consider the
247 complexity of interactions within the oxide film on Fe⁰.

248 **Acknowledgments**

249 Thoughtful comments provided by E.M. Pierce and K. Rod (Pacific Northwest National
250 Laboratory, Richland - USA) on the draft manuscript are gratefully acknowledged. The
251 manuscript was improved by the insightful comments of anonymous reviewers from Journal
252 of Hazardous Materials. The work was partly supported by the Deutsche
253 Forschungsgemeinschaft (DFG-No 626).

254 **References**

- 255 [1] S.F. O'Hannesin, R.W. Gillham, Long-term performance of an in situ "iron wall" for
256 remediation of VOCs. *Ground Water* 36 (1998), 164-170.
- 257 [2] J.L. Jambor, M. Raudsepp, K. Mountjoy, Mineralogy of permeable reactive barriers for
258 the attenuation of subsurface contaminants. *Can. Miner.* 43 (2005), 2117-2140.
- 259 [3] A.D. Henderson, A.H. Demond, Long-term performance of zero-valent iron permeable
260 reactive barriers: a critical review. *Environ. Eng. Sci.* 24 (2007), 401-423.

- 261 [4] L.J. Matheson, P.G. Tratnyek, Reductive dehalogenation of chlorinated methanes by iron
262 metal, *Environ. Sci. Technol.* 28 (1994), 2045–2053.
- 263 [5] C. Noradoun, M.D. Engelman, M. McLaughlin, R. Hutchenson, K. Breen, A.
264 Paszczynski, I.F. Cheng, Destruction of chlorinated phenols by dioxygen activation under
265 aqueous room temperature and pressure conditions. *Ind. Eng. Chem. Res.* 42 (2003), 5024-
266 5030.
- 267 [6] S.H. Joo, A.J. Feitz, T.D. Waite, Oxidative degradation of the carbothioate herbicide,
268 molinate, using nanoscale zero-valent iron. *Environ. Sci. Technol.* 38 (2004), 2242-2247.
- 269 [7] C.E. Noradoun, I.F. Cheng, EDTA degradation induced by oxygen activation in a
270 zerovalent iron/air/water system. *Environ. Sci. Technol.* 39 (2005), 7158-7163.
- 271 [8] C.E. Noradoun, C.S. Mekmaysy, R.M. Hutchenson, I.F. Cheng, Detoxification of
272 malathion a chemical warfare agent analog using oxygen activation at room temperature and
273 pressure. *Green Chem.* 7 (2005), 426-430.
- 274 [9] I. Sanchez, F. Stüber, J. Font, A. Fortuny, A. Fabregat, C. Bengoa, Elimination of phenol
275 and aromatic compounds by zero valent iron and EDTA at low temperature and atmospheric
276 pressure. *Chemosphere* 68 (2007) 338-344.
- 277 [10] I.A. Katsoyiannis, T. Ruettimann, S.J. Hug, pH dependence of fenton reagent generation
278 and As(III) oxidation and removal by corrosion of zero valent iron in aerated water. *Environ.*
279 *Sci. Technol.* (2008), ASAP Web Release Date: 30-Aug-2008.
- 280 [11] O. Gyliene, T. Vengris, A. Stoncius, O. Nivinskiene, Decontamination of solutions
281 containing EDTA using metallic iron. *J. Hazard. Mater.* (2008),
282 doi:10.1016/j.jhazmat.2008.02.066.
- 283 [12] C. Noubactep, Processes of contaminant removal in “Fe⁰-H₂O” systems revisited: The
284 importance of co-precipitation. *Open Environ. J.* 1 (2007), 9-13.

- 285 [13] M.S. Odziemkowski, T.T. Schuhmacher, R.W. Gillham, E.J. Reardon, Mechanism of
286 oxide film formation on iron in simulating groundwater solutions: Raman Spectroscopic
287 studies, *Corr. Sci.* 40 (1998), 371-389.
- 288 [14] B.K. Lavine, G. Auslander, J. Ritter, Polarographic studies of zero valent iron as a
289 reductant for remediation of nitroaromatics in the environment. *Microchem. J.* 70 (2001), 69-
290 83.
- 291 [15] R. Mantha, K.E. Taylor, N. Biswas, J.K. Bewtra, A continuous system for Fe⁰ reduction
292 of nitrobenzene in synthetic wastewater. *Environ. Sci. Technol.* 35 (2001), 3231-3236.
- 293 [16] J.A. Mielczarski, G.M. Atenas, E. Mielczarski, Role of iron surface oxidation layers in
294 decomposition of azo-dye water pollutants in weak acidic solutions. *Applied Catalysis B:
295 Environ.* 56 (2005), 289–303.
- 296 [17] D.F. Laine, I.F. Cheng, The destruction of organic pollutants under mild reaction
297 conditions: A review. *Microchem. J.* 85 (2007), 183-193.
- 298 [18] C. Noubactep, A critical review on the mechanism of contaminant removal in Fe⁰-H₂O
299 systems. *Environ. Technol.* 29 (2008), 909-920.
- 300 [19] C. Noubactep, On the validity of specific rate constants (k_{SA}) in Fe⁰/H₂O systems. *J.*
301 *Hazard. Mater.* (2008) In Press, Accepted Manuscript, Available online 28 August 2008.
- 302 [20] C. Noubactep, On the operating mode of bimetallic systems for environmental
303 remediation. *J. Hazard. Mater.* (2008) In Press, Accepted Manuscript, Available online 13
304 August 2008.
- 305 [21] R.E. Dickerson, H.B. Gray, G.P. Haight, Jr., *Chemical Principles*. 3rd Ed.
306 Benjamin/Cummings Inc., London, 1979.
- 307 [22] J.A. Campbell, *General Chemistry*. 2nd Ed. Springer, Weinheim, 1990 (in German).
- 308 [23] E. Tipping, Some aspects of the interactions between particulate oxides and aquatic
309 humic substances. *Mar. Chem.* 18 (1986), 161-169.

310 [24] R.J. Crawford, I.H. Harding, D.E. Mainwaring, Adsorption and coprecipitation of
311 multiple heavy metal ions onto the hydrated oxides of iron and chromium. *Langmuir* 9
312 (1993), 3057-3062.

313 [25] E.R. Landa, A.H. Le, R.L. Luck, P.J. Yeich, Sorption and coprecipitation of trace
314 concentrations of thorium with various minerals under conditions simulating an acid uranium
315 mill effluent environment, *Inorg. Chim. Acta* 229 (1995), 247-252.

316 [26] T. Nishimura, Y. Umetsu, Oxidative precipitation of arsenic(III) with manganese(II) and
317 iron(II) in dilute acidic solution by ozone, *Hydrometallurgy* 62 (2001), 83-92.

318 [27] U. Schwertmann, F. Wagner, H. Knicker, Ferrihydrite–Humic associations magnetic
319 hyperfine interactions, *Soil Sci. Soc. Am. J.* 69 (2005), 1009-1015.

320 [28] Y. Satoh, K. Kikuchi, S. Kinoshita, H. Sasaki, Potential capacity of coprecipitation of
321 dissolved organic carbon (DOC) with iron(III) precipitates, *Limnology* 7 (2006), 231-235.

322 [29] B. Gu, J. Schmitt, Z. Chen, L. Liang, J.F. McCarthy, Adsorption and desorption of
323 natural organic matter on iron oxide: mechanisms, and models, *Environ Sci Technol* 28
324 (1994), 38-46.

325 [30] K.J. Vetter, General kinetics of passive layers on metals. *Electrochim. Acta* 16 (1971),
326 1923-1937.

327 [31] V.J. Linnenbom, The reaction between iron and water in the absence of oxygen. *J.*
328 *Electrochem. Soc.* 105 (1958), 322-324.

329 [32] L.G. Knowlton, Some experiments on iron, *J. Phys. Chem.* 32 (1928), 1572-1595.

330 [33] J.S. Kim, P.J. Shea, J.E. Yang, J.E. Kim, Halide salts accelerate degradation of high
331 explosives by zerovalent iron, *Environ. Pollut.* 147 (2007), 634-641.

332 [34] X. Liu, F.J. Millero, The solubility of iron hydroxide in sodium chloride solutions.
333 *Geochim. Cosmochim. Acta* 63 (1999), 3487-3497.

334 [35] M.R. Antonio, G.B. Karet, J.P. Guzowski Jr., Iron chemistry in petroleum production.
335 *Fuel* 79 (2000), 37–45.

336 [36] D. Brondel, R. Edwards, A. Hayman, D. Hill, S. Mehta, T. Semerad, Corrosion in the oil
337 industry. *Oilfield Rev.* 6 (1994), 4-18.

338 [37] S. Nestic, F. Carroll, Horizontal rotating cylinder. A compact apparatus for studying the
339 effect of water wetting on carbon dioxide corrosion of mild steel, *Corrosion* 59 (2003), 1085-
340 1095.

341 [38] M. Nordsveen, S. Nestic, R. Nyborg, A. Stangeland, A mechanistic model for carbon
342 dioxide corrosion of mild steel in the presence of protective iron carbonate films - Part 1:
343 Theory and verification. *Corrosion* 59 (2003), 443-456.

344 [39] B. Craig, Corrosion products analyses – A road map to corrosion in oil and gas
345 productions, *Mater. Performance* 41 (2002), 56-58.

346 [40] H.X. Guo, B.T. Lu, J.L. Luo, Interaction of mechanical and electrochemical factors in
347 erosion-corrosion of carbon steel, *Electrochim. Acta* 51 (2005), 315-323.

348 [41] J.D. Miller, L.W. Beckstead, Surface deposit effects in the kinetics of copper
349 cementation by iron, *Metal. Mater. Trans. B* 4 (1973), 1967-1973.

350 [42] V. Annamalai, L.E. Murr, Influence of deposit morphology on the kinetics of copper
351 cementation on pure iron. *Hydrometallurgy* 4 (1979), 57-82.

352 [43] T.E. Shokes, G. Möller, Removal of dissolved heavy metals from acid rock drainage
353 using iron metal, *Environ. Sci. Technol.* 33 (1999), 282-287.

354 [44] Z. Hao, X. Xu, J. Jin, P. He, Y. Liu, D. Wang, Simultaneous removal of nitrate and
355 heavy metals by iron metal, *J. Zhejiang Univ. Sci.* 6B (2005), 353-356.

356 [45] A. Ghauch, Discussion of Chicgoua Noubactep on "Removal of thiobencarb in aqueous
357 solution by zero valent iron" by Md. Nurul Amin et al. [*Chemosphere* 70 (2008) 511-515],
358 *Chemosphere* 72 (2008), 328-331.

359 [46] C. Noubactep, Comments on "Removal of thiobencarb in aqueous solution by zero valent
360 iron" by Md. Nurul Amin et al. [*Chemosphere* 70 (2008) 511-515], *Chemosphere* 72 (2008),
361 325-327.

362 [47] C. Noubactep, G. Meinrath, P. Dietrich, M. Sauter, B. Merkel, Testing the suitability of
363 zerovalent iron materials for reactive walls, *Environ. Chem.* 2 (2005), 71-76.

364 [48] E.M. Pierce, D.M. Wellman, A.M. Lodge, E.A. Rodriguez, Experimental determination
365 of the dissolution kinetics of zero-valent iron in the presence of organic complexants,
366 *Environ. Chem.* 4 (2007), 260-270.

367

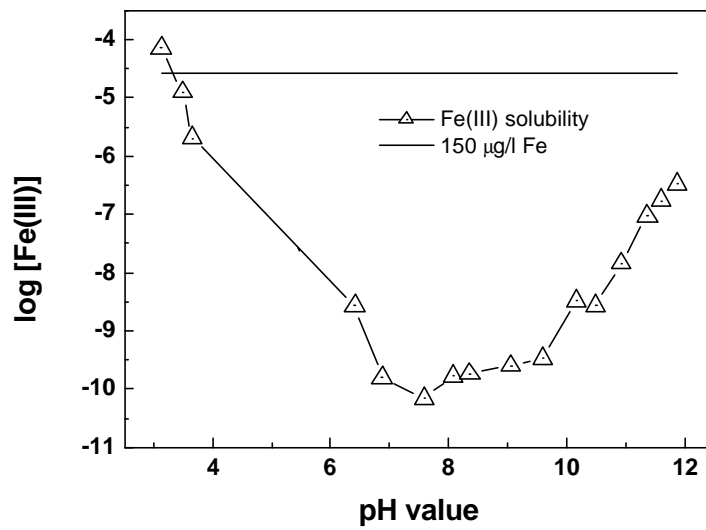
367 **Table 1:** Possible abiotic reaction pathways for contaminant (Ox) removal from groundwater
 368 in a Fe⁰ reactive barrier and their reversibility under natural conditions. FeOOH is a proxy of
 369 corrosion products and Fe_x(OH)_y^(3x-y) is an iron hydroxide. The reversibility is accessed
 370 mostly for degradable organic species. However, even for inorganic species reduction can be
 371 considered irreversible if severe changes do not occur. Modified after ref. [18].

mechanism	reaction	reversibility	Eq.
Fe⁰ reduction	$\text{Fe}^0 + \text{Ox}_{(\text{aq})} \Rightarrow \text{Fe}^{2+} + \text{Red}_{(\text{s or aq})}$	irreversible	(1)
adsorption	$\text{FeOOH} + \text{Ox}_{(\text{aq})} \Leftrightarrow \text{FeOOH-Ox}$	reversible	(2)
co-precipitation	$\text{Ox}_{(\text{aq})} + n \text{Fe}_x(\text{OH})_y^{(3x-y)} \Leftrightarrow \text{Ox}[\text{Fe}_x(\text{OH})_y^{(3x-y)}]_n$	irreversible	(3)
Fe^{II}_(aq) reduction	$\text{Fe}^{\text{II}}_{(\text{aq})} + \text{Ox}_{(\text{aq})} \Rightarrow \text{Fe}^{\text{III}} + \text{Red}_{(\text{s or aq})}$	irreversible	(4)
Fe^{II}_(s) reduction	$\text{Fe}^{\text{II}}_{(\text{s})} + \text{Ox}_{(\text{aq or aq})} \Rightarrow \text{Fe}^{\text{III}} + \text{Red}_{(\text{s or aq})}$	irreversible	(5)
H₂ reduction	$\text{H}_2 + \text{Ox}_{(\text{aq or aq})} \Rightarrow \text{H}^+ + \text{Red}_{(\text{s or aq})}$	irreversible	(6)

372

373

373 Figure 1



374

375 **Figure 1:** Comparison of solubility data of Fe^{III} in 0.01 M NaCl at 25 °C (data from ref. [34])
376 with iron concentration at 1 % iron consumption under the experimental conditions of ref.
377 [10]. It can be seen that contaminant removal experiments are mainly performed under
378 conditions where solubility limits of Fe(OH)₃ have been exceeded. Therefore, it is very likely
379 that contaminants are simply entrapped in the matrix of precipitating iron oxides.

380