1 **Metallic iron for environmental remediation: Back to textbooks**

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10 **Abstract**

11 The use of metallic iron as environmental remediation medium was based on an incorrect

12 interpretation of experimental observations. Since then, faced with seemingly contradictory

13 data, researchers have substantially revised their models but controversial reports are still

14 current, suggesting that a substantial revision is unavoidable. This communication analyses

15 redox processes in Fe^0/H_2O systems and demonstrates that the current paradigm even

16 contradicts textbook knowledge on aqueous iron corrosion that was available before the

17 advent of the Fe^0 technology. Accordingly, the use of metallic iron for environmental

18 remediation should be regarded as a classical case where scientists are entrenched in a false

19 paradigm. An immediate correction is recommended before a questionable 'novelty' is

20 transferred into standard textbooks.

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22 **Keywords**: Chemical Reduction, Electrochemical Reaction, Paradigm shift, Zerovalent iron.

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1   Introduction

Controversy is a part of science but is rarely presented in science textbooks [1-3]. In fact, textbooks mostly present final results in form of established hypotheses and models [4]. This approach has been criticized as learners (e.g. undergraduates) do not access the true nature of science [1-4]. Science is universal knowledge that is conventionally gained in a non-linear 'step-by-step' accumulation process. As a matter of fact, new findings may emerge from unexpected places, and lead to rapid progress in previously unexpected directions [4-6].

The use of metallic iron (Fe^0) for environmental remediation should be regarded as a discovery from an 'unexpected' place [2,7]. In fact, according to textbook knowledge available before the introduction of this technology, Fe^0 would never have been regarded as reducing agent in water at pH > 4.5 and containing micro-amounts of pollutants (micro-pollutants) [8,9]. In other words, no working (electro)chemist would have had the idea to use iron as reducing agent under environmental conditions [10-15]. However, used as reducing agent, Fe^0 has been proven efficient for environmental remediation, wastewater treatment and safe drinking water provision [16-28]. Apart from wastewater treatment, these are typical situations were species of interest are present in trace amounts (micro-pollutants) [29,30]

Over the past two decades, an accumulation of data disapproving the virtually universally accepted idea that Fe^0 is a reducing agent has been observed [6,15,31]. Although the still currently accepted paradigm was disproved five years ago [32,33], it has been largely ignored by working scientists and other practitioners of the Fe^0 technology [34]. This situation suggests ethical issues may not be obligatory in science as giving the state-of-the-art knowledge on any relevant issue should remain a must for any scientific paper [35]. It should be acknowledged that the concept stipulating that Fe^0 is the main reducing agent has never been univocally accepted. Three examples for illustration: (i) Lipczynska-Kochany et al. [10] questioned the long-term efficient of reductive reaction at circumneutral pH, (ii) Odziemkowski et al. [11] demonstrated the impossibility of quantitative reduction of n-

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50 nitrosodimethylamine by Fe^0 under laboratory conditions, and (iii) Farrell et al. [12]

51 demonstrated that under anoxic conditions Fe^0 is quantitatively oxidized by water (H^+).

52 Disregarding any ethical issues, the present communication aims at demonstrating why

53 Fe^0/H_2O systems are good remediation system although Fe^0 is not a reducing agent. The

54 discussion is based on an analysis of the Fe^0/H_2O system under anoxic conditions (Tab. 1)

55 using textbook knowledge available before the introduction of the Fe^0 remediation

56 technology. The basic Fe^0/H_2O system is extended to the redox couple Cu^{II}/Cu^0 and O_2/OH^- to

57 expand the discussion to bimetallic systems and system operating under oxic conditions.

58 Results corroborates that Fe^0 is not likely to serve as a reducing agent.

59 **2   The natural anoxic Fe^0/H_2O system**

60 Natural Fe^0/H_2O systems are defined as Fe^0 in natural waters ($6.5 \leq pH \leq 9.5$). That is water

61 immersed Fe^0 at pH values larger than 5.0. In this pH range, Fe^0 corrosion is dominated by

62 'oxygen adsorption' type meaning that the oxidative agents must come in contact with Fe^0 or

63 a conductive scale at its surface [36-42]. Table 1 summarizes some relevant equations for

64 such a system. Basically, in the absence of oxidizing agents including oxygen (strictly anoxic

65 conditions), there are three inherent redox couples (Fe^{II}/Fe^0, H^I/H^0 and Fe^{III}/Fe^{II}) to be

66 considered (Eq. 1, 2, 3, 5). The likely reactions on a pure thermodynamic perspective are

67 given in Eq. 7 to 10.

68 Aqueous corrosion of Fe^0 materials at pH > 4.5 is an electrochemical process involving the

69 anodic dissolution of iron (Eq. 1) and the cathodic evolution of hydrogen (Eq. 3) [8]. The

70 overall reaction is given by Eq. 7. Eq. 7 alone shows that hydrogen evolution is driven by Fe^0

71 oxidation through water. Accordingly, any attempt to rationalize contaminant reduction by

72 Fe^0 using hydrogen evolution is faulty. However, ideally, Eq. 7 is an equilibrium, meaning

73 that, according to Le Chatellier's principle, if Fe^{2+} is consumed in a chemical reaction (e.g. O_2

74 reduction – Eq. 13), increased H_2 evolution will be observed. This is the fundamental link

75 between 'H_2 evolution' and 'contaminant reduction'. Therefore, increased 'H_2 evolution' in

76 the presence of any contaminant is an indicator for indirect reduction by Fe^{II}. The possibility

77 that the contaminant of concern is rather reduced by H_2 should not be excluded [11]. In this

78 case, recorded H_2 evolution is a fraction of total H_2.

79 Another important feature from Tab. 1 (Eq. 7 to 10) is the variety of Fe^{II} and H_2 sources. In

80 particular H_2 may derive from three different sources: (i) Fe^0 corrosion by water (Eq. 7), (ii)

81 $Fe^0_{(ads)}$ oxidation by water (Eq. 8), and the Shikorr reaction (iii) (Eq. 10). The Shikorr reaction

82 is known to occur at temperatures above 80 °C but could be catalyzed by the presence of Fe^0

83 [43]. On the other hand, beside oxidation of Fe^0 by water (Eq. 7), Fe^{II} could result from Fe^0

84 oxidation by aqueous Fe^{III} (Eq. 9). These additional sources of reducing agents have been

85 largely overseen as contaminant reduction has been mostly attributed to Fe^0 [28,44,45].

86 However, Data from Hydrometallurgy and Synthetic Organic Chemistry have not yet

87 univocally proven the extent of direct reduction (electrons from Fe^0) in chemical reduction

88 involving Fe^0, even at elevated temperatures [45-51]. For example, Gould [46] reported on a

89 reaction stoichiometry of 1.33 mol of dissolved iron per mol of Cr^{VI} reduced. This high

90 efficiency was attributed to generated H_2 acting as a reducing agent for Cr^{VI}. As discussed

91 here, beside H_2, $Fe^{II}_{(ads)}$ and $Fe^{II}_{(aq)}$ are further sources of reducing agents for Cr^{VI} ($E^0 = 1.53$

92 V). Given the possibility that Fe^{II} is 'recycled' by generated Fe^{III} (Eq. 9), discussing the actual

93 reaction stoichiometry is a complex task which is over the scope of this communication. In

94 the real world Fe^{II}-recycling by microbial activity render the system more complex.

95 Accordingly, whether Fe^0 contribute and to which extent to the process of contaminant

96 reduction under anoxic conditions is still unclear. The situation is more complex under oxic

97 conditions.

98 **3   The natural oxic Fe^0/H_2O system**

99 Table 1 shows that all possible reactions under anoxic conditions are possible under oxic

100 conditions as well. In fact, O_2 is a more powerful oxidizing agent than water (H^+ or H_2O). The

101 kinetics of Fe^0 oxidation by O_2 is more rapid. According to Cohen [52] the reaction is 65

102 times more rapid than under anoxic conditions. However, oxidation with O_2 is coupled with

103 the formation of non conductive oxides (e.g. FeOOH, Fe_2O_3) that will impede any electron

104 transfer from Fe^0 (direct reduction). On the other hand, the rapid production of adsorptive

105 species (e.g. $Fe(OH)_2$, FeOOH, Fe_2O_3) is the rationale for increased contaminant removal

106 under oxic conditions [53,54].

107 Under oxic conditions the surface of Fe^0 is rapidly covered with a multi-layered oxide scale

108 through which any species, including O_2, must migrate to reach the Fe^0 surface. It has been

109 traceably demonstrated that, under 'external' oxic conditions, Fe^0 is oxidized by water (Eq. 7)

110 and dissolved O_2 is reduced by Fe^{II} (Eq. 13) [41,42,55]. This suggests that, as long as the

111 oxide scale is porous enough to enable Fe^{II} diffusive transport from the Fe^0 surface to sites

112 within the oxide scale where dissolved oxygen (and any other oxidizing species) can diffuse

113 in the opposite direction, chemical reduction could occur. Whether this chemical reaction is

114 quantitative or not depends on several factors including the intrinsic reactivity of used Fe^0, the

115 flux of oxidizing agent and the water chemistry [32,33,40-42]. These aspects are not further

116 discussed here. It is sufficient to consider, that the observed electrochemical Fe^0 oxidation is

117 not necessarily coupled with species reduction by electrons from Fe^0 (direct reduction).

118 The last important feature from Tab. 1 is the presence of the couple Cu^{II}/Cu^0 which is

119 considered a model alloying element for bimetallic systems. It is clearly seen that water can

120 not oxidize Cu^0 (oxidative dissolution to Cu^{2+}). Accordingly Cu^0 acts as galvanic cell and

121 facilitated Fe^0 oxidative dissolution [9,53,54]. This process accelerates all other processes

122 discussed above. Moreover, under anoxic conditions, Fe^{II} recycling in sustained (Eq. 11).

123 Under oxic conditions, Cu^0 dissolution is induced and resulted Cu^{2+} may sustain Fe^0 oxidation

124 (cementation). All these predictions are in tune with the observed increased efficiency of

125 bimetallic systems. They also corroborate the view that bimetallic systems sustain an indirect

126 reaction between Fe^0 and dissolved species [53,54,57].

4   Discussion

Experience in publishing concepts and results on remediation with Fe^0 shows that authors are regularly referred to the grey literature [34,57]. In particular, ITRC [34] is the fifth document published since 1999 by the Interstate Technology & Regulatory Council (50 F Street, NW, Suite 350, Washington, DC 20001) to investigate the development of Fe^0 permeable reactive barriers as an "emerging remediation technology". However, the fifth edition failed to consider ground-breaking information available in the international literature from 2007 on [32,33,54] and intensively indexed in databases. Even though the content of these 'handbooks' are from renowned scientists and practitioners, it is important that these studies be published in peer-reviewed journals, for example in form of "(Bi-)Annual reviews". This approach will increase the credibility of the contained information and constitute something like an 'authoritative basis' to further shape the design, and management of Fe^0 treatment systems and minimise any negative impacts.

It is important to notice that the Glossary of ref. [34] defines Fe^0 as "a strong reducing agent". While this definition is correct on a pure thermodynamic perspective (E^0 = -0.44 V), under natural situations, Fe^0 is at best a producer of reducing agents (Fe^{II}, green rust, H_2) which are all instable species and are further transformed. Contaminants are certainly removed during this dynamic process [15]. The extent of contaminant chemical reduction, however, is difficult to discuss. Moreover, even reduced species should be removed from the aqueous phase [6,15,58,59]. Relevant contaminant removal mechanisms are adsorption, co-precipitation, and adsorptive size-exclusion [58,59]. Adsorptive size-exclusion refers to the increased straining capacity due to porosity loss. Porosity loss is inherent to Fe^0 filtration bed because iron corrosion is expansive in nature. In fact, the volume of each corrosion product (e.g. FeO, Fe_3O_4, Fe_2O_3, $FeOOH$, $Fe(OH)_3$) is 2.1 to 6.4 times larger that the volume of a Fe atom [60-64].

152 Irrespective from the availability of handbooks, any researcher starting in a new domain has

153 to find his way in a jungle information. A good path is to start with textbooks, then read

154 review articles (e.g. from databases) and then repeat some relevant experiments to test

155 reproducibility before start own experiments. Testing repeatability includes verifying the

156 correctness of mathematical equations. If this 'basic' approach were generally used, a false

157 premise would not have survived for 20 years in an active field of research with actually more

158 than 1500 peer-reviewed articles (Tab. 2).

159 Since 1994 research within the field of "Fe^0 technology" has boomed. On April 1st 2012, a

160 search at "ACS publications", "Science Direct" (Elsevier journals), "Springer journals", and

161 "Wiley journals" using the key word "zero-valent iron" suggested that up to 1871 peer-

162 reviewed articles may have been published (Tab. 2). This clearly demonstrates the interest

163 within academia for this technology. Accordingly, it is urgent that active research is done on a

164 common basis.

165 The elevated proportion of scientists currently ignoring the state-of-the-art knowledge on

166 remediation with Fe^0 is reflected in Tab. 2 (also see ref. [65]). While some 1871 articles may

167 have been published on remediation with Fe^0, only some 273 have referenced 'Noubactep'.

168 Considering only the year 2011 at Elsevier, Noubactep has been referenced 37 times in 84

169 articles on "zero-valent iron" and "water", this clearly shows that more than 50 % of all

170 publications ignores the current state-of-the-art knowledge on 'Fe^0 remediation'. Moreover,

171 journal manuscripts and grant proposals will continue to be rejected by established 'experts',

172 the sole 'curses' of the applicants being to have been: (i) assiduous students trying to realize

173 knowledge from their undergraduate lessons, or (ii) creative graduates willing to experience

174 what should be 'inherent in research science': creativity [4].

175 The history of science is full of examples of primarily rejected ground-breaking ideas [66].

176 For example, Avogadro's hypothesis that equal volumes of all gases, under the same

177 temperature/pressure conditions, contain equal numbers of molecules was initially rejected.

178   This hypothesis was later proven of key importance in solving many problems in chemical

179   sciences. To date, the view that Fe^0 is mostly a generator of reducing agents (H_2 and Fe^{II}) and

180   Fe oxides has been either severely refuted or just tolerated [67-73]. The tolerance is based on

181   the simplification that, without Fe^0, no secondary reducing agents could be available.

182   Accordingly, Fe^0 serves as the original source of electron donors (H, H_2 and Fe^{II}). The present

183   communication has refuted the named simplification and established that quantitative

184   reduction can only result from secondary reducing agents. Accepting this 'evidence' is a

185   prerequisite for further technology development. In fact, designing a system in which

186   contaminant reduction should be mediated by a surface reaction is different from designing a

187   system for continuous iron corrosion, sufficient to warrant contaminant removal by

188   adsorption, co-precipitation and size-exclusion.

189   **5   Concluding remarks**

190   This communication is an expansion of some earlier ideas summarized in Noubactep [51].

191   The overall goal is to demonstrate that progress in 'iron for environmental remediation' cannot

192   be achieved if the theory of the system is not established. The way forward is to revise the

193   view that Fe^0 is a reducing agent. The alternative view, that Fe^0 is a producer of contaminant

194   'scavengers', is in tune with textbook knowledge available before the discovery of this

195   efficient technology. The alternative theory explained better how contaminant removal is

196   achieved. Testing protocols for Fe^0 materials [74] and experimental protocols for contaminant

197   removal [75-77] are also provided. When extensively tested these protocols will allow rapid

198   progress of the Fe^0 remediation technology. Moreover, this science-based approach will ease

199   the general technology acceptance. The participation of the entire community is required.

200   In closing, it is wished that more attention is paid to theoretical works in Environmental

201   Sciences. This is indeed a major requirement for creativity inherent in research [4,78]. The

202   effectiveness of the current data-based approach is clearly underscored. Data should only be

203   produced to fill gap of knowledge. Actually the current approach has led to the fact that

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204 'knowledge' disproving textbooks has been accepted for 20 years. Moreover, proofs are

205 requested from any 'dissidents' as if the aqueous iron corrosion was a new discovery. Given

206 the broad consensus on this false premise [77,79,80], it is important that the mistake is

207 corrected before Fe^0 is presented in standard textbooks as a 'reducing agent' for

208 environmental remediation.

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418

418 **Table 1**: Standard electrode potentials of the Fe^0/H_2O system and some relevant related

419 reactions. Apart from $Fe^{III}_{(ads)}/Fe^{II}_{(ads)}$ all electrode potentials are arranged in increasing order

420 of E^0. The higher the E^0 value, the stronger the reducing capacity of Fe^0 for the oxidant of a

421 couple. The couples Cu^{II}/Cu^0 (Eq. 4) and O^0/O^{-II} (Eq. 6) are considered to discuss the cases of

422 bimetallic systems and reactions under oxic conditions respectively.

Chemical reaction			E^0 (V)	Eq.
$Fe^0_{(s)}$	$\Leftrightarrow$	$Fe^{2+}_{(aq)} + 2\ e^-$	-0.44	(1)
$Fe^{2+}_{(ads)}$	$\Leftrightarrow$	$Fe^{3+}_{(ads)} + e^-$	-0.34/-0.65	(2)
$H^+ + e^-$	$\Leftrightarrow$	$\frac{1}{2}\ H_{2(g)}$	0.00	(3)
$Cu^0_{(s)}$	$\Leftrightarrow$	$Cu^{2+}_{(aq)} + 2\ e^-$	0.34	(4)
$Fe^{2+}_{(aq)}$	$\Leftrightarrow$	$Fe^{3+}_{(aq)} + e^-$	0.77	(5)
$O_2 + 2\ H_2O + 4\ e^-$	$\Leftrightarrow$	$4\ OH^-$	0.81	(6)
Reactions under anoxic conditions				
$Fe^0_{(s)} + 2\ H^+$	$\Rightarrow$	$Fe^{2+}_{(aq)} + H_{2(g)}$		(7)
$Fe^{2+}_{(ads)} + H^+$	$\Rightarrow$	$Fe^{3+}_{(ads)} + \frac{1}{2}\ H_{2(g)}$		(8)
$Fe^0_{(s)} + 2\ Fe^{3+}_{(aq)}$	$\Rightarrow$	$3\ Fe^{2+}_{(aq)}$		(9)
$3\ Fe(OH)_{2(s)}$	$\Rightarrow$	$Fe_3O_{4(s)} + H_{2(g)} + 2\ H_2O$		(10)
$Cu^0_{(s)} + 2\ Fe^{3+}_{(aq)}$	$\Rightarrow$	$Cu^{2+}_{(aq)} + 2\ Fe^{2+}_{(aq)}$		(11)
Reactions under oxic conditions				
$Fe^0_{(s)} + \frac{1}{2}\ O_2 + H_2O$	$\Rightarrow$	$Fe^{2+}_{(aq)} + 2\ HO^-$		(12)
$2\ Fe^{2+} + \frac{1}{2}\ O_2 + H_2O$	$\Rightarrow$	$2\ Fe^{3+}_{(aq)} + 2\ HO^-$		(13)
$Cu^0_{(s)} + \frac{1}{2}\ O_2 + H_2O$	$\Rightarrow$	$Cu^{2+}_{(aq)} + 2\ HO^-$		(14)

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424

424   **Table 2**: Results of a web-search for "Zero-valent iron" and "Noubactep" at four relevant

425   publishers demonstrating the current interest within academia for the Fe^0 technology (search:

426   01 April 2012). The results for "Noubactep" was corrected to consider only the publication

427   directly dealing with 'Fe^0 remediation'.

428

Publisher	ZVI	Noubactep
ACS publications	491	19
Elsevier Journals	492	190
Springer Journals	380	40
Wiley Journals	508	24
Total	1871	273

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