

1                   **Water remediation by metallic iron: Much ado about nothing –**  
2                   **As profitless as water in a sieve?**

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12 **Running title:** Interdisciplinary approach gone astray? Save the peer-review system.  
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27 **Water remediation by metallic iron: Much ado about nothing - As profitless as water in**  
28 **a sieve?**

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35 There has been much ado about water treatment with metallic iron ( $\text{Fe}^0$ ) since the early 1990s.  
36 Thousands of articles, books, papers and technical reports have been written (i) describing  
37 laboratory feasibility tests, pilot plant performances and field implementations from around  
38 the world, (ii) outlining fundamental causes of failure (if applicable), and (iii) suggesting  
39 changes for more efficient  $\text{Fe}^0$  systems [1,2]. However, crucial knowledge about the operating  
40 mode of  $\text{Fe}^0$ -based systems is still lacking. In other words, fundamental knowledge necessary  
41 for the proper design of more efficient  $\text{Fe}^0$  remediation systems is still largely ignored [3].  
42 To fill this knowledge gap and exploit the huge potential of  $\text{Fe}^0$  for water treatment, it is  
43 urgent to use a scientifically-based, truly interdisciplinary approach. Such a comprehensive,  
44 holistic and inclusive approach will unify a sound community in the quest of more efficient  
45  $\text{Fe}^0$  remediation systems. This argumentation is not new as the funding policy of several  
46 agencies is based on 'interdisciplinary approach'. In other words, an interdisciplinary  
47 approach is already largely followed. Yet still severe crises are encountered, in particular  
48 concerning the mechanism of contaminant removal in  $\text{Fe}^0/\text{H}_2\text{O}$  systems or even, concerning  
49 the intrinsic nature of  $\text{Fe}^0$ . Is  $\text{Fe}^0$  a stand-alone reducing agent or a parent of (adsorbing,  
50 enmeshing and) reducing agents? The discussion on the nature of  $\text{Fe}^0$  is now lasting more  
51 than 6 years [4] but is still largely profitless. It seems, there is a lack of willingness to test new  
52 ideas even though the comfortable one is obviously not efficient.

53 The technology of treating water with  $\text{Fe}^0$  was born with the spurious perception, that  $\text{Fe}^0$  is a  
54 reducing agent [5]. This illusive view would have challenged almost a 200-years-old  
55 knowledge on the electrochemical nature of aqueous corrosion [6,7] and almost 100 years  
56 expertise from intensive research on aqueous iron corrosion [8]. In 1923, Ulick Richardson  
57 Evans (1889-1980) has provided a modern understanding of the corrosion process based on  
58 the electrochemical theory. Fortunately, the pioneers of the technology have not explicitly  
59 challenged the electrochemical theory of aqueous iron corrosion. They have simply ignored it  
60 and built a self-satisfactorily ‘knowledge system’ regarding  $\text{Fe}^0$  as a reducing agent. This  
61 knowledge system can not explain why chemical species without any redox properties have  
62 been quantitatively removed in  $\text{Fe}^0/\text{H}_2\text{O}$  systems. Moreover, for  $\text{Fe}^0$  to act as a reducing  
63 agent, electrons from the metal body should be relayed to the species of concern (including  
64 contaminants) by electronic conductive phases [5]. However, neither the multi-layer oxide  
65 scale on iron is conductive nor natural organic materials have been (univocally) positively  
66 tested as ‘electron shuttles’ [9-13]. In fact, the model of oxide scale generation and evolution  
67 sustaining the ‘reductive transformation’ concept [9] was proven inconsistent by  
68 Odziemkowski and colleagues [10-12]. Moreover, although magnetite films ( $\text{Fe}_3\text{O}_4$ ) are  
69 electronic conductive in nature, the whole oxide scale on  $\text{Fe}^0$  is always made of several layers  
70 including layers of  $\text{Fe}^{\text{III}}$ -species [14-16]. This evidence makes quantitative electron transfer  
71 from the metal body to species adsorbed at the outer surface of the oxide scale unlikely. In  
72 other words, all ‘crutches’ that have supported the introduction of the illusive concept have  
73 been proven false, but the concept is still miraculously alive.

74 A cursory look at the literature on remediation with  $\text{Fe}^0$  reveals a vast scholarship originating  
75 from diverse disciplines and using  $\text{Fe}^0$  of various types and sizes for multiple goals (e.g.  
76 environmental remediation, drinking water production, soil cleaning, wastewater treatment)  
77 [17-19]. The acronym “zero-valent iron” is used to designate elemental/metallic iron. That is  
78 iron in the oxidation state zero ( $\text{Fe}^0$ ). The term ‘valence’ in “zero-valent iron” is wrongly

79 used. This misleading acronym is anterior to the  $\text{Fe}^0$  remediation technology. However,  $\text{Fe}^0$  is  
80 (still almost) univocally used as electron source for contaminant reductive transformation.  
81 Current and past researches aim to improve the understanding of interactions within the  
82  $\text{Fe}^0/\text{H}_2\text{O}$  system, such that more efficient systems could be designed. It is obvious that no real  
83 improvement is possible when the intrinsic nature of  $\text{Fe}^0$  is not established/recognized [20].  
84 The intrinsic nature of aqueous metal corrosion is summarized in a paper by Sato [21] in the  
85 following terms: “*Metallic corrosion produces a layer of corrosion precipitates on the metal*  
86 *surface in aqueous solutions. The interfacial layer thus produced influences the corrosion of*  
87 *underlying metals depending on its ionic and electronic properties. The presence of a gel-like*  
88 *or porous precipitate layer of insoluble rusts such as hydrous metal salts or oxides causes*  
89 *either accelerated metallic corrosion or passivation”*. This text recalls that iron is corroded by  
90 water and that the  $\text{Fe}^0$  surface is covered by oxide layers. These layers are non conductive as a  
91 rule. Accordingly, regardless from the background of any active researcher, his primary work  
92 should consist on elucidating how such a system will behave in the presence of target species,  
93 including the contaminants. If such an approach was adopted, a false concept would have not  
94 been introduced in the 1990s. Moreover, an alternative view would have not remain 7 years  
95 mostly untested.

96 Arguments against the alternative view are numerous and include the following: (i) the  
97 prevailing concept is well accepted, (ii) it is not worth to look nearly into the matter, (iii) the  
98 author has not presented experimental results, (iv) the author has already published this  
99 argument in other forums, (v) no better support of old arguments are given, and (vi) related  
100 articles appeared in ‘low impact journal’. Taken together this argumentation is not based on  
101 scientific facts and has even not really addressed the crucial point: the reductive  
102 transformation concept is simply false. The best pseudo-scientific argument will not correct  
103 this mistake. A more scientific attitude recommends that the inherently wrong concept is

104 abandoned and the alternative, already positively tested by few researchers [20,22-24] is  
105 considered as the new compass in exploring the Fe<sup>0</sup>/H<sub>2</sub>O universe.

106 There is indeed much ado about the operating mode of Fe<sup>0</sup>/H<sub>2</sub>O systems, as there should be.  
107 The critical issue of this discussion is the mechanism of contaminant removal. This issue is  
108 elegantly solved by simply properly considering the iron corrosion literature [14-16].  
109 Alternatively, the thermodynamics of iron oxidative dissolution and the subsequent  
110 precipitation of iron phases can be considered. Instead of arguing with examples, scientists  
111 should have trusted the expertise of their colleagues who are closer in their academic  
112 background to electrochemistry [25,26]. Thus, it is argued that the operating mode of Fe<sup>0</sup>/H<sub>2</sub>O  
113 systems must be addressed comprehensively through sound interdisciplinary studies. In this  
114 effort, expertise of individual scientists should be respected. If individual expertise is not  
115 respected, the vast array of ‘scientific’ studies may just seep through the sieve of intellectual  
116 selfishness. This intellectual selfishness is as profitless as water in a sieve [27,28].

117 To conclude, the German thinker, Johann Wolfgang von Goethe (28.08.1749 - 22.03.1832)  
118 will be quoted: *“In the sciences, people quickly come to regard as their own personal  
119 property that which they have learned and had passed on to them at the universities and  
120 academies. If someone else comes along with new ideas that contradict the Credo and in fact  
121 even threaten to overturn it, then all passions are raised against this threat and no method is  
122 left untried to suppress it. People resist it in every way possible: pretending not to have heard  
123 about it; speaking disparagingly of it, as if it were not even worth the effort of looking into the  
124 matter. And so a new truth can have a long wait before finally being accepted.”* It is amazing,  
125 perhaps also surprising, to realize that this observation is valid even for an evidence resulting  
126 from a falsification of the mainstream corrosion science. It seems that the primordial  
127 motivation for scientific publication is no more the scientific content but some common  
128 ‘urgencies’ (“publish or perish”). Relevant ‘urgencies’ include patents, promotions, proposal  
129 success or salary increments [29]. “Publish or perish” is an excellent threatening reminder of

130 the importance of the publication of scientific achievements. However, despite simplified  
131 accessibility to scientific articles (e.g. SciFinder<sup>®</sup>, Scopus<sup>®</sup>, Web of Sciences<sup>®</sup>) dealing with  
132 Fe<sup>0</sup>, individual articles must be critically and impartially evaluated. In other words, the “So  
133 what?” question [30] should always be in the mind of each author, if scientific progress is  
134 sought.

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### 140 **References**

- 141 [1] D. H. Phillips, T. Van Nooten, L. Bastiaens, M. I. Russell, K. Dickson, S. Plant, J. M. E.  
142 Ahad, T. Newton, T. Elliot, R. M. Kalin, Ten year performance evaluation of a field-scale  
143 zero-valent iron permeable reactive barrier installed to remediate trichloroethene  
144 contaminated groundwater. *Environ. Sci. Technol.* **2010**, *44*, 3861–3869.
- 145 [2] R. T. Wilkin, S. D. Acree, R. R. Ross, R. W. Puls, T. R. Lee, L. L. Woods, Fifteen-year  
146 assessment of a permeable reactive barrier for treatment of chromate and trichloroethylene  
147 in groundwater. *Sci. Tot. Environ.* **2014**, *468–469*, 186–194.
- 148 [3] C. Noubactep, Aqueous contaminant removal by metallic iron: Is the paradigm shifting?  
149 *Water SA* **2011**, *37*, 419–426.
- 150 [4] C. Noubactep, Processes of contaminant removal in “Fe<sup>0</sup>–H<sub>2</sub>O” systems revisited. The  
151 importance of co-precipitation. *Open Environ. J.* **2007**, *1*, 9–13.
- 152 [5] E.J. Weber, Iron-mediated reductive transformations: investigation of reaction  
153 mechanism. *Environ. Sci. Technol.* **1996**, *30*, 716–719.
- 154 [6] A. De la Rive, **1830**, citation after Roberge [7].

- 155 [7] P. R. Roberge, *Handbook of corrosion engineering*. McGraw-Hill New York/San  
156 Francisco, **2000**, 1130 pp.
- 157 [8] U. R. Evans, *An Introduction to Metallic Corrosion*. London, Edward Arnold Ltd., 3rd  
158 ed., **1981**, 302 pp.
- 159 [9] M.M. Scherer, S. Richter, R.L. Valentine, P.J.J. Alvarez, Chemistry and microbiology of  
160 permeable reactive barriers for in situ groundwater clean up. *Rev. Environ. Sci. Technol.*  
161 **2000**, *30*, 363–411.
- 162 [10] K. Ritter, M.S. Odziemkowski, R.W. Gillham, An in situ study of the role of surface  
163 films on granular iron in the permeable iron wall technology. *J. Contam. Hydrol.* **2002**,  
164 *55*, 87–111.
- 165 [11] M.S. Odziemkowski, R.P. Simpraga, Distribution of oxides on iron materials used for  
166 remediation of organic groundwater contaminants - Implications for hydrogen evolution  
167 reactions. *Can. J. Chem.* **2004**, *82*, 1495–1506.
- 168 [12] M. Odziemkowski, Spectroscopic studies and reactions of corrosion products at surfaces  
169 and electrodes. *Spectrosc. Prop. Inorg. Organomet. Compd.* **2009**, *40*, 385–450.
- 170 [13] F. Fu, W. Han, B. Tang, M. Hu, Z. Cheng, Insights into environmental remediation of  
171 heavy metal and organic pollutants: Simultaneous removal of hexavalent chromium and  
172 dye from wastewater by zero-valent iron with ligand-enhanced reactivity. *Chem. Eng. J.*  
173 **2013**, *232*, 534–540.
- 174 [14] M. Cohen, The formation and properties of passive films on iron. *Can. J. Chem.* **1959**,  
175 *37*, 286–291.
- 176 [15] M. Cohen, Thin oxide films on iron. *J. Electrochem. Soc.* **1974**, *121*, 191C–197C.
- 177 [16] S. Nestic, Key issues related to modelling of internal corrosion of oil and gas pipelines –  
178 A review. *Corros. Sci.* **2007**, *49*, 4308–4338.

- 179 [17] S. Comba, A. Di Molfetta, R. Sethi, A Comparison between field applications of nano-,  
180 micro-, and millimetric zero-valent iron for the remediation of contaminated aquifers.  
181 *Water Air Soil Pollut.* **2011**, 215, 595–607.
- 182 [18] M. Gheju, Hexavalent chromium reduction with zero-valent iron (ZVI) in aquatic  
183 systems. *Water Air Soil Pollut.* **2011**, 222, 103–148.
- 184 [19] A. Ghauch, G. Ayoub, S. Naim, Degradation of sulfamethoxazole by persulfate assisted  
185 micrometric Fe<sup>0</sup> in aqueous solution. *Chem. Eng. J.* **2013**, 228, 1168–1181.
- 186 [20] K. Miyajima, *Optimizing the design of metallic iron filters for water treatment*. Freiberg  
187 Online Geoscience **2012**, 32, 60 pp.
- 188 [21] N. Sato, Surface oxides affecting metallic corrosion. *Corros. Rev.* **2001**, 19, 253–272.
- 189 [22] M. Gheju, I. Balcu, Removal of chromium from Cr(VI) polluted wastewaters by  
190 reduction with scrap iron and subsequent precipitation of resulted cations. *J. Hazard.*  
191 *Mater.* **2011**, 196, 131–138.
- 192 [23] S. Bilardi, P.S. Calabrò, S. Caré, N. Moraci, C. Noubactep, Improving the sustainability  
193 of granular iron/pumice systems for water treatment. *J. Environ. Manage.* **2013**, 121,  
194 133–141.
- 195 [24] A. Ghauch, Iron-based metallic systems: An excellent choice for sustainable water  
196 treatment. Habilitation Thesis, University of Grenoble, France, **2013**.
- 197 [25] E. Lipczynska-Kochany, S. Harms, R. Milburn, G. Sprah, N. Nadarajah, Degradation of  
198 carbon tetrachloride in the presence of iron and sulphur containing compounds.  
199 *Chemosphere* **1994**, 29, 1477–1489.
- 200 [26] B. K. Lavine, G. Auslander, J. Ritter, Polarographic studies of zero valent iron as a  
201 reductant for remediation of nitroaromatics in the environment. *Microchem. J.* **2001**, 70,  
202 69–83.
- 203 [27] W. Shakespeare, *Much Ado About Nothing*. citation after Tobin [18].



- 204 [28] G.A. Tobin, Water promises: Much ado about nothing - as profitless as water in a sieve?  
205 *J. Contemp. Water Res. Educ.* **2009**, *142*, 1–3.
- 206 [29] J.L. Schnoor, Announcing Environmental Science & Technology Letters. *Environ. Sci.*  
207 *Technol.* **2013**, *47*, 7579–7579.
- 208 [30] A. Berthod, So What? or required content of a review article. *Sep. Purif. Rev.* **2009**, *38*,  
209 203–206.