

1 **Metallic iron for water treatment: A knowledge system challenges mainstream science**

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10
11 **Abstract**

12 A knowledge system (KS) is a knowledge that is unique to a given group of persons. This
13 form of knowledge may have a local or natural origin and is linked to the community that has
14 produced it. On the contrary, the core of mainstream science (MS) is the desire to profoundly
15 understand processes, through sequential studies such as hypothesis formulation, experiment
16 and prediction. Thus, KS is communitarian and MS is universal. KS can be understood and
17 rendered universal through MS. In general, a process discovery (know-how) may be intuitive,
18 accidental, conjectural or inspirational but outcomes should be predictable and repeatable as
19 soon as the know-why is achieved by MS. This paper argues that the technology of using
20 metallic iron for water treatment has all the characteristics of a KS and that promoters of this
21 technology have deliberately rejected scientific arguments leading to the know-why of the
22 fortuitous discovery. Consequently, the technology has developed into an impasse where
23 controversial discoveries are reported on all relevant aspects. It is concluded that the integrity
24 of science is endangered by this communitarian behaviour.

25 **Keywords:** False premise, Knowledge system, Mainstream science, Peer review, Zerovalent
26 iron.

27 **1 Introduction**

28 The use of elemental iron (Fe^0) for water treatment has attracted much attention thanks to its
29 great potential for removing several classes of substances from the aqueous phase [1-9]. Fe^0
30 has been proven the most efficient material for subsurface reactive permeable barriers
31 (reactive walls) [6, 10, 11]. Actually, there are about 180 Fe^0 reactive walls installed
32 worldwide [6]. The large majority of them been meeting their design goals.

33 The use of Fe^0 in reactive walls was discovered around 1990 as summarized in ref. [6].
34 Gillham and his colleagues [12] fortuitously found that trichloroethylene was reduced in a
35 steel canister. This result was reproducible. Subsequent "laboratory testing and verification"
36 experiments were performed [13-15]. To understand the importance of this discovery, one
37 should consider that chlorinated organic compounds are more toxic and less biodegradable
38 than their non-chlorinated reduction products. Accordingly, reducing chlorinated organic
39 compounds is an ideal way to make them less toxic and more biodegradable. The discovery of
40 Gillham et al. [12] coincided with the active search of appropriate materials for reactive walls
41 after the concept for groundwater remediation presented by McMurty and Elton [16]. From
42 1990 on, Fe^0 has been tested at several scales and is now an established technology for water
43 treatment (groundwater remediation, wastewater treatment, safe drinking water production)
44 [4, 5, 7-9, 11]. However, despite observed efficiency, the Fe^0 reactive wall technology as a
45 whole is based on a false premise which should be clarified before the technology develops
46 properly.

47 The objective of this communication is to demonstrate that leading scientists or research
48 groups working on "water treatment with Fe^0 " are too confident with the false premise that
49 iron is a reducing agent for contaminant reductive transformations. Accordingly, each
50 alternative concept is systematically disregarded, endangering the integrity of science and
51 questioning the efficiency of the peer review system. For the sake of clarity, the popular state-

52 of-the-art knowledge on the mechanism of contaminant removal in Fe⁰/H₂O systems will first
53 be presented.

54 **2 Mechanism of contaminant removal**

55 Since the introduction of Fe⁰ bed filtration technology for groundwater remediation, several
56 contaminants and contaminant groups have been reported to be removed by reductive
57 transformations [17-19]. Clearly, contaminants were considered to be removed because of
58 their chemical transformations possibly making them less harmful (reductive degradation) or
59 less mobile (reductive precipitation). Accordingly, the case for which reduction products are
60 toxic is still actively discussed [20]. Moreover, the formation of the universal oxide film on
61 Fe⁰ (reactivity loss) and the pore filling by iron corrosion products (permeability loss) have
62 been regarded as the major inhibitive factors for the process of contaminant removal [3, 21-
63 23].

64 The formation of the universal oxide film at the surface of Fe⁰ is a characteristic of iron
65 corrosion at pH > 4.5 [24, 25]. The film results from the precipitation of iron (hydr)oxides at
66 the surface or in the vicinity of Fe⁰. In separating Fe⁰ from water, the formed porous film
67 necessarily lowers the kinetic of iron oxidation. On the other hand, the permeability loss
68 results from the expansive nature of iron corrosion. In fact, upon corrosion, the volume of
69 formed iron oxide is 2.08 to 6.40 times larger than the volume of the parent metal (V₀) in the
70 lattice (Fe⁰) [26,27]. The volumetric expansion (ΔV - Eq. 1) corresponds to the extent of
71 porosity loss.

$$72 \quad \Delta V = (\eta - 1) * V_0 \quad (1)$$

73 Where $2.08 \leq \eta \leq 6.40$.

74 The hitherto presentation shows that three major opened questions of the Fe⁰ technology are:
75 (i) how can harmful reaction products be removed? (**Question 1**) (ii) how can reactivity loss
76 be prevented? (**Question 2**) and how can permeability loss be properly considered? (**Question**
77 **3**) Answering these three questions will accelerate technology development and could open

78 new perspectives. However, it is not likely that the popular state-of-the-art knowledge
79 presented above will enable the adequate search of answers because it has neglected several
80 key aspects. It should be emphasized that Question 2 and Question 3 have been recently
81 theoretically addressed. It was shown that mixing Fe^0 (< 52 vol-%) with inert or reactive but
82 non expansive additive will sustain long term corrosion and prolong Fe^0 bed's lifespan [28,
83 29]

84 **3 Fundamental flaws of the current accepted mechanism**

85 The premise that aqueous contaminants are reduced by Fe^0 is founded on the thermodynamic
86 instability of Fe^0 in aqueous solutions (immersed iron corrosion). Accordingly, all oxidized
87 contaminants which electrode potential is larger than that of Fe^0 ($E_{\text{Fe}^{2+}/\text{Fe}^0}^0 = -0.44 \text{ V}$) should
88 be reduced by Fe^0 . However, water (H_2O or $\text{H}^+ - E_{\text{H}^+/\text{H}_2}^0 = 0.0 \text{ V}$) as solvent is also corrosive
89 for Fe^0 and is present in stoichiometric abundance. Accordingly, irrespective from the
90 presence of any reducible species (including dissolved oxygen and contaminants), water will
91 oxidize Fe^0 . This reaction can not be considered a side reaction as has been mistakenly done
92 [17] (**Mistake 1**). Moreover, it is the oxidation of Fe^0 by water that produces the oxide scale
93 responsible for the reported reactivity loss. Accordingly, reactivity loss is an inherent property
94 of Fe^0 and should properly considered if Fe^0 is to be used in aqueous solutions (at $\text{pH} > 4.5$).
95 In this respect, enhancing the reactivity of Fe^0 by reducing its particle size (μm and nm) for
96 example will not avoid the formation of the universal oxide scale. The oxide scale is
97 necessarily a diffusion barrier for all dissolved species as its shields the Fe^0 surface [24, 25].
98 Note that the initial oxide scale is porous alloying retarded transport of water and dissolved
99 species including Fe^{II} , H/H_2 and eventually molecular O_2 . The initial porous film may develop
100 to an impervious one which stops corrosion. The process of film formation is rigorously the
101 same under anoxic and oxic conditions. The major difference being the kinetics. According to
102 Cohen [25] the film forms 65 times slower under anoxic conditions. Given that adsorbed Fe^{II}
103 and H/H_2 are powerful reducing agents, they will more likely contribute to contaminant

104 reduction (if applicable) than the surface of Fe^0 [30]. Accordingly, even when contaminant
105 reduction is quantitative, effective reducing agents are likely primary iron corrosion products
106 (indirect reduction by Fe^{II} and H/H_2) (**Mistake 2**).

107 The paramount mistake (**Mistake 3**) has been to confound “contaminant removal” and
108 “contaminant reduction”. The goal of water treatment is contaminant removal and it is very
109 difficult to say whether the reduction of a species has been achieved by electrons from Fe^0 ,
110 Fe^{II} or H/H_2 (direct or indirect reduction). It is clear that a reduced contaminant should be
111 removed from water to obtain clean water. The five major contaminant removal mechanisms
112 in Fe^0 beds are: adsorption, co-precipitation, precipitation, size-exclusion and volatilization.
113 Biological and chemical transformations could influence the removal capability of a
114 substance but are not removal mechanisms. Accordingly, **Question 1** (how can harmful
115 reaction products be removed? – Section 2) should be revisited because contaminants and
116 transformation products should be removed from the aqueous phase. Moreover, contaminant
117 transformation products have been removed from the aqueous phase, unless the technology
118 would have not been efficient. The problem is that “contaminant removal” and “contaminant
119 reduction” were randomly interchanged.

120 The hitherto presentation has unmasked the popular state-of-the-art knowledge on the process
121 of aqueous contaminant removal by Fe^0 as non accurate. This false premise is well-accepted
122 and repeated in the introduction of many articles and books. The question arises why the
123 technology is efficient.

124 **4 The real mechanism of contaminant removal in $\text{Fe}^0/\text{H}_2\text{O}$ systems**

125 The real mechanism of aqueous contaminant removal in the presence of Fe^0 (e.g. $\text{Fe}^0/\text{H}_2\text{O}$
126 systems) can be derived from the pH dependence of the solubility of iron (Fe^{II} , Fe^{III}) in
127 aqueous solutions (Fig. 1) [31-33]. In other words, Fe^0 can be regarded as generator for Fe
128 species and the behaviour of these species used to discuss the efficiency of contaminant
129 removal. In this case, the major question for $\text{Fe}^0/\text{H}_2\text{O}$ sustainability is how to maintain the

130 corrosion process? (**Question 4**). Answering Question 4 is over the scope of this
131 communication. However, it should be noticed that the continuation of the corrosion process
132 depends on the porosity of the initial oxide scale on Fe^0 [34]. In other words, answering
133 Question 4 will consist in investigating the effects of operational conditions on the porosity of
134 the oxide scale in long-term experiments. In such experiments, the oxide scale should allow to
135 form and transform on the surface of Fe^0 (no or slow agitation, shaking or stirring).
136 Figure 1 shows clearly, that for $\text{pH} > 5$ the solubility of Fe under oxic conditions is smaller
137 than 10^{-5} M (0.56 mg). Under anoxic conditions, Fe^{II} has a relatively high solubility. The
138 saturation concentration of Fe^{II} species approaches 0.5 M (28 g/L) at room temperature.
139 However, dissolved Fe concentrations drop below 10^{-12} M (5.6×10^{-11} g/L) if Fe^{II} is
140 polymerized e.g. $[\text{Fe}(\text{OH})_2]_n$ or oxidized to Fe^{III} species [35]. This reaction results in the
141 precipitation of Fe phases. Fe^{III} species can also form under anoxic conditions, for example,
142 when water contains oxidizing species like NO_3^- , MnO_2 or MnOOH . Fe^{II} oxidation and Fe
143 phase formation is often catalyzed by microorganisms. Fe^{III} phases which form from solution
144 begin as small clusters that evolve into larger polymeric units with time, eventually reaching
145 colloidal sizes [36]. Contaminants are necessarily enmeshed in the matrix of corrosion Fe
146 phases and/or adsorbed at their surface [37, 38]. Adsorbed or enmeshed contaminants can be
147 further reduced by diffusing Fe^{II} and H/H_2 . Reduced contaminants will be
148 adsorbed/enmeshed. That is the way contaminants have been successfully removed in
149 $\text{Fe}^0/\text{H}_2\text{O}$ systems [39, 40]. This statement is supported by results of some few authors (e.g.
150 ref. [41-45]), but the validity of the reductive transformation concept has never been
151 systematically questioned. For example, Furukawa et al. [43] stated that “the ubiquitous
152 presence of ferrihydrite suggests that the use of Fe^0 -PRBs may be extended to applications
153 that require contaminant adsorption rather than, or in addition to, redox-promoted
154 contaminant degradation”. Jia et al. [44] used Fe^0 as adsorbent generator of the removal of
155 non-reducible organic species (triazoles). The new concept stipulates that adsorption and co-

156 precipitation are the fundamental mechanism of contaminant removal, regardless of the redox
157 properties.

158 It is very important to note that contaminants are not removed by Fe^0 or individual Fe phases
159 but by the whole process of aqueous iron corrosion in a porous system (e.g. bed, wall) [39,
160 40]. Although this plausible explanation is compatible with the open literature on the
161 interaction of iron oxides with contaminants in the hydrosphere as recently demonstrated [7,
162 40], some leading scientists [46-48] are continuing to defend the false premise with
163 supposedly scientific arguments [49, 50]. This attitude has degraded the research community
164 on Fe^0 to a sort of modern communitarian knowledge system.

165 **5 A modern knowledge system**

166 Currently the expression *knowledge system* is used in the scientific literature to describe
167 efficient knowledge that has been used by small communities in the third world and by
168 indigenous peoples in North America and Australia [51-55]. According to Mapara [55],
169 indigenous knowledge systems (IKS) are bodies of knowledge of the indigenous people of
170 particular geographical areas that have survived on for a very long time. They are knowledge
171 forms that have failed to die despite colonial onslaught and scholar arrogance [55]. In social
172 science, it is commonplace to scientifically investigate a IKS in order to extent its
173 applicability [55, 56]. Sometimes, despite proven amelioration of IKS by mainstream science,
174 indigenous people are not ready to modify their original knowledge unless its holistic socio-
175 cultural and spiritual dimensions are conserved.

176 Presently, the same trend is observed in using Fe^0 for water treatment as demonstrated above.
177 Whatever modern experimental tools have demonstrated to sustain the false premise, the
178 objective of investigations were falsified and/or good results were misinterpreted. There is no
179 need to multiply examples. Interested readers are referred to two recent articles [57, 58]. The
180 sole example will be that of efforts to establish a mass balance to demonstrate the efficiency
181 of Fe^0 to reduce contaminants [59]. In real systems contaminants are removed within the

182 oxide scale on Fe⁰. It is not likely that water will release enmeshed contaminants because
183 water can not dissolve iron oxides [60]. Accordingly, researchers reporting on mass balance
184 without dissolving corrosion products have necessarily done something wrong like
185 mechanically stirring the solution [59].

186 The fact that many researchers are confident to this modern knowledge system is related by
187 the huge number of peer review articles, that have been published on this topic during the last
188 17 years (from 1994 on). Peer review is the process that requires experts in a given field to
189 evaluate an author's work and ideas in that same field, usually for the purpose of publishing a
190 paper or awarding a grant [61]. Considering this definition, it is fair to say that experts in the
191 field of water treatment with Fe⁰ have built a "modern knowledge system" which is now
192 challenging mainstream science. It is superfluous to recall that good manuscripts and
193 proposals have been rejected, the curse of their authors being to think outside of the box.

194 **6 Concluding remarks**

195 The present communication has recalled the danger of the expert feedback system when peer
196 reviewers are not competent. The situation is exacerbated when a college of experts has been
197 built around a false premise for years (yet two decades) [62]. During this time at least four
198 generations of PhD students have spent their youth working on an idea defying mainstream
199 science. This harsh criticism is not to make colleagues look bad, but rather to question the
200 efficiency of the interdisciplinary approach. Iron corrosion is an old research field, where
201 chemists, electrochemists, physicists have controversially discussed for decades [34, 63-65].
202 It is not likely that researchers without good chemical background will understand the
203 important features of iron corrosion without guidance.

204 The process of discovery may be intuitive, accidental, conjectural or inspirational but
205 outcomes should be developed to predictable and repeatable issues. Despite 20 years of
206 intensive research, no repeatable or predictable results have been achieved while using
207 metallic iron for water treatment [57, 58]. Accordingly the whole achieved results is highly

208 qualitative. Furthermore, all existing models for the process of contaminant removal in
209 Fe⁰/H₂O systems are faulty as none up to date properly considers the fundamental process of
210 co-precipitation. To exploit the huge potential of Fe⁰ for environmental remediation and safe
211 drinking water provision, a concerted research scientific effort is needed [39, 67-70]. The first
212 step to this great future will be to abandon false premises and develop the actual
213 communitarian knowledge system to a real scientific community.

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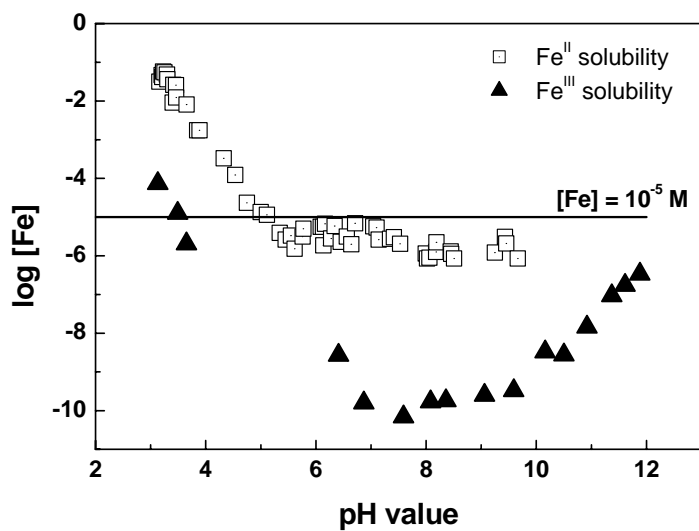
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380 **Fig. 1:** Solubility data of Fe^{II} in 0.1 M NaCl (25 °C) and Fe^{III} in 0.01 M NaCl (25 °C) as a
381 function of pH. Data for Fe^{II} are from ref. [33] and data for Fe^{III} from ref. [31].

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