

# 1                                    **Relevant reducing agents in remediation Fe<sup>0</sup>/H<sub>2</sub>O systems**

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## 7    **Abstract**

8    Metallic iron (Fe<sup>0</sup>) is often reported as a reducing agent for environmental remediation. There  
9    is still controversy as to whether Fe<sup>0</sup> plays any significant direct role in the process of  
10    contaminant reductive transformation. The view that Fe<sup>0</sup> is mostly a generator of reducing  
11    agents (e.g. H, H<sub>2</sub> and Fe<sup>II</sup>) and Fe oxyhydroxides has been either severely refuted or just  
12    tolerated. The tolerance is based on the simplification that, without Fe<sup>0</sup>, no secondary  
13    reducing agents could be available. Accordingly, Fe<sup>0</sup> serves as the original source of electron  
14    donors (including H, H<sub>2</sub> and Fe<sup>II</sup>). The objective of this communication is to refute the named  
15    simplification and establish that quantitative reduction results from secondary reducing  
16    agents. For this purpose, reports on aqueous contaminant removal by Al<sup>0</sup>, Fe<sup>0</sup> and Zn<sup>0</sup> are  
17    comparatively discussed. Results indicated that reduction may be quantitative in aqueous  
18    systems containing Fe<sup>0</sup> and Zn<sup>0</sup> while no significant reduction is observed in Al<sup>0</sup>/H<sub>2</sub>O  
19    systems. Given that Al<sup>0</sup> is a stronger reducing agent than Fe<sup>0</sup> and Zn<sup>0</sup>, it is concluded that  
20    contaminant reduction in Fe<sup>0</sup>/H<sub>2</sub>O systems results from synergic interactions between H/H<sub>2</sub>  
21    and Fe<sup>II</sup> within porous Fe oxyhydroxides. This conclusion corroborates the operating mode of  
22    Fe<sup>0</sup> bimetallics as H/H<sub>2</sub> producing systems for indirect contaminant reduction.

23    **Keywords:** Adsorption, Contaminant removal, Mechanisms, Reduction, Zerovalent metals.

## 24 **1 Introduction**

25 Permeable reactive barriers (or reactive walls) containing metallic iron ( $\text{Fe}^0$ ) as reactive  
26 medium is an established technology for passive groundwater remediation [1-17].  $\text{Fe}^0$  media  
27 have been intensively investigated at laboratory, pilot- and full-scale for the remediation of  
28 various groups of reducible contaminants including chlorinated solvents, nitroaromatic  
29 compounds, petroleum hydrocarbon, heavy metals, and radionuclides [4,11,14,18].  
30 Quantitative removal of non-reducible contaminants (e.g.  $\text{Zn}^{\text{II}}$ ) [19] and micro-organisms  
31 [20,21] has also been documented. Thus, more than a 'simple' reducing agent,  $\text{Fe}^0$  should be  
32 regarded as a universal material for aqueous contaminant removal [16,22-26]. The fact that  
33 contaminant reduction and contaminant removal should not be randomly interchanged has  
34 been already discussed [27-34]. Accordingly, while quantitative contaminant removal is  
35 certain, the extent of contaminant reduction (if applicable) is difficult to assess/discuss  
36 without quantitative speciation and dissolution of iron corrosion products [35-37]. As an  
37 example, Lee et al. [38] reported that 'no carbon balances between reactants and products  
38 have ever been successfully done for many chlorinated hydrocarbons'. Lee et al. [38]  
39 concluded that this was an indication that the reductive transformation of these contaminants  
40 is not fully understood. Therefore, the environmental safety of reaction products may be still  
41 unclear [39,40]. Recent developments in understanding the mechanism of contaminant  
42 removal in  $\text{Fe}^0/\text{H}_2\text{O}$  systems have shown that original contaminants and their reduction  
43 products are basically removed by unspecific mechanisms (co-precipitation, size exclusion)  
44 inherent to aqueous iron corrosion at pH values characteristic for natural waters [27-29,41-  
45 47].

46 Based on the premise that  $\text{Fe}^0$  is a reducing agent, other metallic elements, including  $\text{Al}^0$ ,  $\text{Cu}^0$ ,  
47  $\text{Sn}^0$ ,  $\text{Ti}^0$  and  $\text{Zn}^0$  have been (or are currently) tested as alternative barrier materials [48-56].  
48 However, the development status for individual metallic elements, including  $\text{Fe}^0$ , is difficult  
49 to assess. Moreover, it is difficult to relate available information to design criteria because

50 experiments are often designed with own past experience or rules of thumb [15,17,57], mostly  
51 using Fe<sup>0</sup>/systems as reference. The difficulty arises from the fact that there is neither a  
52 reference Fe<sup>0</sup> material nor a standard protocol to test Fe<sup>0</sup> materials.

53 There are repeated claims that the adsorption/co-precipitation concept [27,41,42] for  
54 contaminant removal in Fe<sup>0</sup>/H<sub>2</sub>O systems has been introduced by prolifically refuting  
55 extensive work validating the still prevailing reductive degradation/precipitation concept  
56 [58,59] without any original experimental work [60-64]. Thus, the adsorption/co-precipitation  
57 concept has been mostly ignored by the scientific community. Unfortunately, this  
58 argumentation ignored seven important facts: (i) the reductive degradation/precipitation  
59 concept has never been univocally accepted [39,65-67], (ii) the author of the adsorption/co-  
60 precipitation concept has initially published on the reductive precipitation by Fe<sup>0</sup> using  
61 uranium as model contaminant [68], (iii) intensive work with methylene blue as model  
62 contaminant has disproved the reductive degradation/precipitation concept [69-71], (iv) apart  
63 from Ghauch and his colleagues [61] no other researcher or research group who has initially  
64 criticized the adsorption/co-precipitation concept has poised to test it, (v) Ghauch et al. [43-  
65 45] have validated the adsorption/co-precipitation concept using various organic pollutants  
66 including clofibric acid and diclofenac, (vi) chemical reduction is definitively not a stand  
67 alone removal mechanism for any contaminant [17,28,30,32,47], and (vii) the incriminated  
68 prolific literature is a peer-reviewed one. To sum up, the adsorption/co-precipitation concept  
69 is currently dismissed because the reductive degradation/precipitation concept is widely  
70 accepted [62] or because no laboratory or field work with chlorinated organic compounds has  
71 been published to support it [63,64]. This attitude has virtually divided the research  
72 community into two schools (pro and contra one of the concepts), although the adsorption/co-  
73 precipitation concept was clearly introduced as an extension of the then (and still) prevailing  
74 reductive degradation/precipitation concept while explaining several reported discrepancies  
75 [41,42].

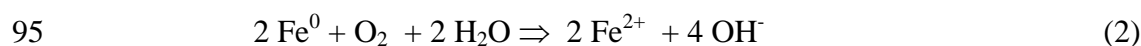
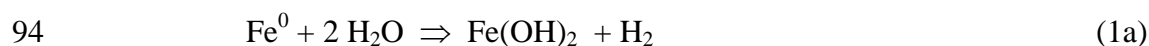
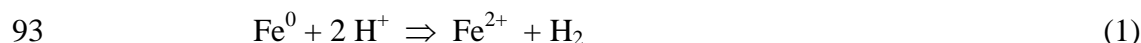
76 The present communication aims at further elucidating the contribution of Fe<sup>0</sup> in the process  
77 of contaminant reduction in Fe<sup>0</sup>/H<sub>2</sub>O systems. For this purpose Al<sup>0</sup>/H<sub>2</sub>O, Fe<sup>0</sup>/H<sub>2</sub>O and  
78 Zn<sup>0</sup>/H<sub>2</sub>O systems are comparatively discussed for their contaminant removal and their  
79 contaminant reducing capacity. For the sake of clarity the thermodynamics of involved  
80 systems will be first discussed.

## 81 **2 Thermodynamics of metal/H<sub>2</sub>O systems**

82 This section will comparatively discuss the thermodynamics of processes occurring in  
83 metal/H<sub>2</sub>O systems (M<sup>0</sup>/H<sub>2</sub>O systems) and relevant for metal reactivity yielding contaminant  
84 removal. These processes include: (i) M<sup>0</sup> oxidative dissolution or M<sup>0</sup> corrosion, primarily  
85 yielding metal hydroxides, (ii) M hydroxide stability (solubility or precipitation), and (iii) the  
86 kinetics of the formation of an oxide scale on M<sup>0</sup> surface and its relation to M<sup>0</sup> protectiveness  
87 against further corrosion.

### 88 **2.1 Metal oxidative dissolution**

89 Aqueous M<sup>0</sup> corrosion is essentially an electrochemical process (redox reaction) involving the  
90 anodic dissolution of M<sup>0</sup> and an appropriated cathodic reduction. For natural waters the two  
91 main cathodic reduction reactions are H<sup>+</sup> reduction (or H<sub>2</sub> evolution – Eq. 1, 1a) and O<sub>2</sub>  
92 reduction (O<sub>2</sub> adsorption – Eq. 2), depending on the pH value [72-74].



96 As a rule H<sub>2</sub> evolution is characteristic for low pH values (≤ 4.0) and O<sub>2</sub> adsorption for higher  
97 pH value (> 4.0). However, both cathodic reactions occur to different extents or with different  
98 kinetics at all pH values [75,76]. In particular, O<sub>2</sub> adsorption (pH > 4.0) is accompanied by  
99 metal oxyhydroxide precipitation [74,77,78]. The pH range of natural waters (4 ≤ pH ≤ 10) is  
100 exactly the area of remediation with M<sup>0</sup>/H<sub>2</sub>O systems and corresponds to slow dissolution

101 kinetics of  $\text{Al}^0$ ,  $\text{Fe}^0$  and  $\text{Zn}^0$ . These slow dissolution kinetics are coupled to the low solubility  
102 of Al, Fe and Zn in this pH range, as will be discussed in the next section.

103 Table 1 summarizes the standard electrode potentials of water constituents ( $\text{H}^+$ ,  $\text{O}_2$ ) and  
104 relevant redox couples for  $\text{Al}^0/\text{H}_2\text{O}$  ( $\text{Al}^{\text{III}}/\text{Al}^0$ ),  $\text{Fe}^0/\text{H}_2\text{O}$  ( $\text{Fe}^{\text{II}}/\text{Fe}^0$  and  $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ ), and  $\text{Zn}^0/\text{H}_2\text{O}$   
105 ( $\text{Zn}^{\text{II}}/\text{Zn}^0$ ) systems [79]. It can be seen from Tab.1 that  $\text{Al}^0$  is a stronger reducing agent than  
106  $\text{Zn}^0$  and  $\text{Fe}^0$ . On the other hand, Fe is available in aqueous systems in two different oxidation  
107 states (II, III) while dissolved Al and Zn are available only in one oxidation state (III and II  
108 respectively). Another feature from Tab. 1 is that,  $\text{Al}^0$  and  $\text{Zn}^0$  may be oxidized by  $\text{Fe}^{\text{II}}_{(\text{aq or s})}$ ,  
109  $\text{Fe}^{\text{III}}_{(\text{aq or s})}$ ,  $\text{H}_2$  and  $\text{OH}^-$  while  $\text{Fe}^0$  may be oxidized by  $\text{Fe}^{\text{III}}_{(\text{aq or s})}$ ,  $\text{H}_2$  and  $\text{OH}^-$  [80]. Thus, in  
110  $\text{Al}^0/\text{Fe}^0$  and  $\text{Zn}^0/\text{Fe}^0$  bimetallic systems, apart from electrochemical cells between Al/Zn and  
111 Fe,  $\text{Fe}^0$  dissolution is additionally sustained by species that are produced by the oxidation of  
112 Al/Zn [47]. Remember that the primary iron corrosion products are  $\text{Fe}^{\text{II}}$  and  $\text{H}/\text{H}_2$ . From the  
113  $E^0$  values in Tab. 1 the following increasing order of reactivity of discussed metals is:  $\text{Fe}^0 <$   
114  $\text{Zn}^0 < \text{Al}^0$ . But in all three systems atomic and/or molecular hydrogen ( $\text{H}/\text{H}_2$ ) are further  
115 potential reducing agents whose contribution to contaminant reduction should be properly  
116 considered [65]. Given that  $\text{H}/\text{H}_2$  production is coupled to metal oxidation, the order of  
117 reactivity by  $\text{H}/\text{H}_2$  will be the same as the one given on the basis of the  $E^0$  values. However,  
118 for  $\text{H}/\text{H}_2$  contaminant reduction is an indirect process as metal is oxidized by water ( $\text{H}^+$ ) and  
119 contaminants are reduced by a product of water reduction ( $\text{H}/\text{H}_2$ ).

120 The next important feature of discussed  $\text{M}^0/\text{H}_2\text{O}$  systems is the presence of metal oxides (in-  
121 situ generated corrosion products). Al, Fe and Zn oxyhydroxides are basically good  
122 adsorbents for dissolved species. Al and Fe oxyhydroxides have been successfully used in  
123 drinking water treatment plants [81-85]. The adsorptive characteristics of metal  
124 oxyhydroxides encompass the adsorption of  $\text{Fe}^{\text{II}}$  and  $\text{H}/\text{H}_2$  yielding the powerful reducing  
125 agent ( $\text{Fe}^{\text{II}}_{(\text{s})}$  and  $\text{H}_{(\text{s})}$ ) as discussed in the literature [39,58]. In particular the use of  $\text{Fe}^{\text{II}}_{(\text{s})}$  for  
126 contaminant reductive transformation has been extensively investigated during the past two

127 decades [86-93]. While  $H_{(s)}$  may be formed in all three systems discussed here, only the  
 128  $Fe^0/H_2O$  system is rich in a third reducing agent ( $Fe^{II}_{(s)}$ ) [80]. As a consequence, it can be  
 129 postulated that any anomaly in the behaviour of the  $Fe^0/H_2O$  system compared to the two  
 130 other systems is ascribed to the presence of  $Fe^{II}_{(s)}$  (and to a limited extent to  $Fe^{II}_{(aq)}$ ). It is the  
 131 objective of this communication to demonstrate that contaminant reduction in  $Fe^0/H_2O$   
 132 systems under groundwater conditions is mostly driven within the oxide scale on  $Fe^0$  by  $Fe^{II}_{(s)}$   
 133 and  $H_{(s)}$ . For this purpose the importance of the rate of mass transfer within the oxide scale  
 134 will be presented.

## 135 2.2 The solubility of metal hydroxides

136 The thermodynamic equilibria involved in metal hydroxide precipitation at the  $M^0$  surface can  
 137 be expressed as [78]:



140 The pH value or the concentration of  $H^+$  (or  $OH^-$ ) (Eq. 10) is determinant for the  $K_s$  value (Eq.  
 141 11). The solubility of studied metal hydroxides at pH 7 are given in Tab. 2 and their pH  
 142 dependence illustrated in Fig. 1. The values for Fig. 1 were calculated using OLI Stream  
 143 Analyser which uses the revised Helgeson–Kirkham–Flowers model for the calculation of  
 144 standard thermodynamic properties of aqueous species and the frameworks of Bromley,  
 145 Zemaitis, Pitzer, Debye-Huckel, and others for the excess terms [94-96].

146 Figure 1 shows that Zn is the most soluble metal for the pH values relevant for natural  
 147 situations ( $4.5 \leq pH \leq 9.5$ ). The behaviour of Fe is strongly dependant on the redox  
 148 conditions. Under anoxic conditions,  $Fe^{II}$  is the dominant species and its solubility is even  
 149 higher than that of  $Zn^{2+}$ . For both species however, the solubility is essentially decreased by  
 150 polymer formation such that the actual solubility is considerably smaller than under  
 151 laboratory conditions [9,97]. The solubility of Al is the lowest around pH 6. Under oxic  
 152 conditions,  $Fe^{III}$  is the dominant species and its solubility in the pH range of natural waters is

153 almost constant and equal to  $10^{-7.5}$  M ( $\text{mol L}^{-1}$ ). For  $\text{pH} > 7.5$ , Al is more soluble than Fe,  
154 suggesting that using  $\text{Al}^0$  as groundwater remediation medium could yield elevated dissolved  
155 Al. The situation is even worse for Zn. The presentation above suggests that, in the  
156 perspective of obtaining a metal free water, two situations must be discussed: (i) under anoxic  
157 conditions  $\text{Al}^0$  is the best reactive medium, and (ii) under oxic conditions  $\text{Fe}^0$  is the best  
158 reactive medium.

159 Actually, the goal of groundwater remediation using reduced metals including  $\text{Al}^0$ ,  $\text{Fe}^0$  and  
160  $\text{Zn}^0$  is to exploit the oxidative capacity of these metals in passive systems (no energy input,  
161 little maintenance) for the long term. In other words, contaminant reduction/removal coupled  
162 to metal corrosion should work alone for up to more than four decades [11,14]. For this  
163 operation to be successful, the extent of metal oxidation should not be strongly inhibited by  
164 metal oxyhydroxide precipitation. That is, metal oxides should be as soluble as possible. In  
165 this regard the general increasing order of suitability is  $\text{Al}^0 < \text{Zn}^0 < \text{Fe}^0$ . Under oxic  
166 conditions, a pH-dependent inversion occurs for Al and Fe for  $\text{pH} > 7.5$ . Considering further  
167 the strong decrease of solubility of  $\text{Fe}(\text{OH})_2$  upon polymer formation, the actual general trend  
168 could be:  $\text{Al}^0 < \text{Fe}^0 < \text{Zn}^0$ .

169 In natural waters, electrochemical metal corrosion is always accompanied by the formation of  
170 scales of: (i)  $\text{Al}_2\text{O}_3$  on  $\text{Al}^0$ , (ii) mixed oxides including  $\text{FeOOH}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$  or green rusts  
171 on  $\text{Fe}^0$ , and (iii)  $\text{ZnO}$  on  $\text{Zn}^0$ . The extent to which these scales inhibit further corrosion is  
172 known as protectiveness and will be discussed in the next section. In general,  $\text{Al}_2\text{O}_3$  on  $\text{Al}^0$   
173 and  $\text{ZnO}$  on  $\text{Zn}^0$  are mostly protective and mixed oxides on  $\text{Fe}^0$  are mostly non-protective.

### 174 **2.3 Protectiveness of oxide scale on metals**

175 When the solubility of a metal hydroxide  $[\text{M}(\text{OH})_n]$  is exceeded, it precipitates [76,78].  
176 Precipitation of hydroxides necessarily leads to the formation of an oxide scale on  $\text{M}^0$  upon  
177 hydroxide transformation. A hydroxide scale on  $\text{M}^0$  can slow down the corrosion process by:  
178 (i) presenting a diffusion barrier for the species involved in the corrosion process, and (ii)

179 covering a portion of  $M^0$  surface. As a rule the initial hydroxide scale is porous and thus non-  
180 protective.

181 Hydroxide scales growth extent and their protectiveness depend primarily on the precipitation  
182 rate. As the  $M^0$  surface corrodes under the scale, corrosion continuously undermines the scale.  
183 As voids are created, they are filled up by the ongoing hydroxide precipitation and so on.  
184 When the rate of hydroxide precipitation at the  $M^0$  surface exceeds the rate of metal  
185 dissolution ( $M^0$  corrosion) dense protective scales form. Vice versa, when the corrosion  
186 process undermines the newly formed scale faster than precipitation can fill in the voids, a  
187 porous and non-protective scale forms [76].

188 The presentation above suggests that, thermodynamically more favourable dissolution  
189 reactions are more likely to yield protective hydroxide scales. Accordingly, under identical  
190 conditions (e.g. temperature, water chemistry) the general trend for increasing order of  
191 protective scale formation is  $Fe^0 < Zn^0 < Al^0$ . In other words, given that the process of  
192 oxidative  $M^0$  dissolution is inhibited by the process of hydroxide precipitation,  $Fe^0$  is more  
193 suitable than  $Zn^0$  and  $Al^0$  for long-term passive dissolution (coupled to contaminant removal).  
194 Because metal hydroxides (e.g.  $Fe(OH)_2$ ,  $Fe(OH)_3$ ) are further transformed to metal oxides  
195 (e.g.  $Fe_3O_4$ ,  $Fe_2O_3$ ) (Tab. 2), the compatibility between the crystal structure of metals and  
196 oxides could help to discuss the adhesion of oxides to the surface of metal as adhesive oxide  
197 are non permeable [97].

198 A look on the crystal structures of aluminium, iron and their oxides reveals that the unit-cell  
199 in  $Al^0$  and  $Al_2O_3$  are very similar to one another; thus the formed  $Al_2O_3$  at the  $Al^0$  surface  
200 adhere tightly to  $Al^0$  beneath it. The oxidized surface provides a protective layer that prevents  
201 water and dissolved species from getting to the  $Al^0$  surface. The situation is similar with  $Zn^0$   
202 and  $ZnO$ . The unit-cell of  $Fe^0$  and Fe-oxides ( $FeO$ ,  $FeOOH$ ,  $Fe_2O_3$ ,  $Fe_3O_4$ ) are not particularly  
203 closed [98]. There is no tendency for an iron oxide layer to adhere to  $Fe^0$ . Accordingly,  $Fe^0$   
204 corrosion continues because formed oxide layers are porous and non adherent (thus non-



205 protective). This is the reason why despite thermodynamic prediction (Tab. 1),  $\text{Fe}^0$  is more  
206 suitable than  $\text{Al}^0$  and  $\text{Zn}^0$  for environmental remediation [29]. It should be explicitly recalled  
207 that  $\text{Fe}^0$  is also the sole metal yielding multivalent ions ( $\text{Fe}^{\text{II}}$  and  $\text{Fe}^{\text{III}}$ ) upon oxidation. The co-  
208 existence of  $\text{Fe}^{\text{II}}$  and  $\text{Fe}^{\text{III}}$  in the oxide scale is an argument against an impervious oxide scale.

#### 209 **2.4 Partial conclusion**

210 The present section has demonstrated the synergistic contributions of the thermodynamics of  
211  $\text{M}^0$  corrosion, M hydroxide precipitation and relative structure of  $\text{M}^0$  and M oxides for the  
212 long term reactivity of reduced metals for water treatment. It is shown that despite high  
213 electrode potential ( $E^0$  value, Tab. 1)  $\text{Fe}^0$  is more suitable for long term stand alone reactivity  
214 thanks of the non-protectiveness of the iron oxide scale on  $\text{Fe}^0$ . This scale is made up of  
215 mixtures of iron oxide which are initially very porous and whose porosity may decrease with  
216 age. The change in  $\text{Fe}^0$  reactivity is not roughly attributed to the formation of an oxide scale  
217 [8] but to evolution of its porosity. Thus, the mass transfer of species across the oxide scale is  
218 determinant to identify the relevance of individual reducing agent in the process of  
219 contaminant removal.

#### 220 **3 The importance of mass transfer rate**

221 There is an agreement on the crucial importance of oxide scales on  $\text{Fe}^0$  for the process of  
222 contaminant removal in  $\text{Fe}^0/\text{H}_2\text{O}$  systems [3,41,42,99]. However, there is a net discrepancy on  
223 the role of the oxide scale on the mechanism of contaminant removal [3,99].

224 The popular view is that  $\text{Fe}^0$  acts as a reducing agent (direct reduction) and the oxide film acts  
225 as ‘mediator’ in the process of contaminant reduction [3,83,100]. Accordingly, three possible  
226 functions have been attributed to the oxide scale: (i) the oxide scale may serve as a physical  
227 barrier inhibiting electron transfer from  $\text{Fe}^0$  to reducible species. The electron transfer (direct  
228 reduction) may occur through defects like pits; (ii) the oxide scale may mediate electron  
229 transfer from  $\text{Fe}^0$  to reducible species by acting as a semiconductor (direct reduction); (iii) the  
230 oxide scale may act as a coordinating surface containing sites of  $\text{Fe}^{\text{II}}$  that complexes (indirect

231 reduction). The presentation above has neglected the reducing role of H/H<sub>2</sub>. Recently  
232 however, Jiao et al. [39] have traceably demonstrated that the reduction of carbon  
233 tetrachloride in Fe<sup>0</sup>/H<sub>2</sub>O systems is not a direct reduction (electrons from Fe<sup>0</sup>) but mostly  
234 resulted from adsorbed H. In other words, Fe<sup>0</sup> serves as the original source of electron donors  
235 (H/H<sub>2</sub> and Fe<sup>II</sup>) but is not the immediate electron donor. On the other hand, this model ignored  
236 the fact that iron corrosion products are generated in-situ in the presence of contaminants.  
237 Under such circumstances contaminant enmeshment is inevitable [84,101,102]. This  
238 observation has led to the actual concept for rationalizing the process of contaminant removal  
239 in Fe<sup>0</sup>/H<sub>2</sub>O systems [28-34,41,42].

240 The most recent concept attributes a more important role to oxide scale on Fe<sup>0</sup>. Fe<sup>0</sup>/H<sub>2</sub>O  
241 systems are regarded as domains of precipitating iron hydroxides and contaminants entering  
242 this domain are enmeshed by a primary non-specific mechanism [41,42]. It is well-known,  
243 that the initial oxide scale on Fe<sup>0</sup> is porous and thus permeable to water and dissolves species.  
244 The initial porous scale may be transformed to an impervious one [76]. However, in ideal  
245 situations, the dynamic process of Fe<sup>0</sup> oxidative dissolution will continue until Fe<sup>0</sup> is depleted.  
246 The question is how to dimension a Fe<sup>0</sup>/H<sub>2</sub>O system to achieve satisfactorily contaminant  
247 mitigation? The answer to this question depends on several factors including Fe<sup>0</sup> intrinsic  
248 reactivity, nature of contaminants, O<sub>2</sub> availability, water chemistry, water flow rate and bed  
249 thickness.

250 For the design of a Fe<sup>0</sup> reactive wall, it is fundamental to know the mass transfer rate which is  
251 determinant to accurately size the wall. That is to select the Fe<sup>0</sup> amount and the wall thickness  
252 as function of water flow rate to achieve satisfactorily residence time for contaminant  
253 removal. However, available reaction rates were not consistent between reports because of  
254 differential Fe<sup>0</sup> intrinsic reactivity and differential mixing conditions (mass transfer rate) used  
255 [38,103,104].

256 The paramount significance of mixing conditions is due to the fact that mixing significantly  
257 influences: (i) the rate of  $\text{Fe}^0$  dissolution by transporting resulting  $\text{Fe}^{\text{II}}$ , and (ii) the spatial  
258 location of iron hydroxide precipitation as its production in the vicinity of  $\text{Fe}^0$  is avoid at high  
259 mixing intensities. In other words, while mixing solutions to shorten experimental duration  
260 for investigations in  $\text{Fe}^0/\text{H}_2\text{O}$  systems, serious biases may be introduced that completely  
261 change the nature of the system [41,42,103,104]. Experimental conditions relevant for field  
262 situations, should enable the formation and transformation of Fe oxyhydroxides (oxide scale)  
263 in the vicinity of  $\text{Fe}^0$ . Under such conditions, the synergic effects probably yielding  
264 quantitative contaminant removal by adsorption, adsorptive size-exclusion, co-precipitation or  
265 enmeshment are likely to be simulated. According to Noubactep [41,42] these conditions are  
266 achieved the best under non-disturbed conditions or under shaking intensities lower than 50  
267  $\text{min}^{-1}$  [103,104]. The next section will comparatively discuss the mechanism of contaminant  
268 removal in  $\text{Al}^0/\text{H}_2\text{O}$ ,  $\text{Fe}^0/\text{H}_2\text{O}$  and  $\text{Zn}^0/\text{H}_2\text{O}$  systems in order to identify the role of  $\text{Fe}^0$  in the  
269 process of contaminant removal under conditions relevant to subsurface reactive wall  
270 situations. A succinct state-of-the-art knowledge on the process of aqueous contaminant  
271 removal by  $\text{Al}^0$  and  $\text{Zn}^0$  is presented in the Appendix.

#### 272 **4 Mechanism of contaminant removal $\text{Fe}^0/\text{H}_2\text{O}$ systems**

273 For the discussion of the process of contaminant removal in  $\text{Al}^0/\text{H}_2\text{O}$ ,  $\text{Fe}^0/\text{H}_2\text{O}$  and  $\text{Zn}^0/\text{H}_2\text{O}$   
274 systems, an arbitrary contaminant having an electrode potential higher than that of dissolved  
275 oxygen ( $E^0 > 0.81 \text{ V}$ ) should be selected (Tab. 1). This is to account for the large spectrum of  
276 redox conditions that could be encountered in individual systems. Two possible examples are  
277 chromium ( $\text{Cr}^{\text{VI}}$ ) and perchlorate ( $\text{ClO}_4^-$ ). While  $\text{Cr}^{\text{VI}}$  ( $E^0 = 1.51 \text{ V}$ ) is readily reduced by  $\text{Fe}^{\text{II}}$   
278 and  $\text{Fe}^0$ , the reduction of  $\text{ClO}_4^-$  ( $E^0 = 1.29 \text{ V}$ ) by all three reducing agents has been reported to  
279 be very slow [82,83,85,105-107]. Accordingly, the discussion will be performed on  $\text{ClO}_4^-$   
280 removal. The suitability of dissolved  $\text{ClO}_4^-$  for this study is due to his high stability in non-

281 acidic aqueous solutions. In fact,  $\text{ClO}_4^-$  behaves as an inert electrolyte in chemical and  
282 electrochemical studies [85,105].

283 Table 3 summarizes the results of published works on the mechanism of aqueous  $\text{ClO}_4^-$   
284 removal under ambient conditions by  $\text{Al}^0$ ,  $\text{Fe}^0$  and  $\text{Zn}^0$ . The general trend is that  $\text{ClO}_4^-$   
285 removal is incomplete. Values of removal efficiencies are not added in Tab. 3 because  
286 available results are not directly comparable due to differences in the operational design. In  
287 general quantitative  $\text{ClO}_4^-$  removal is obtained under extreme conditions such as: (i) elevated  
288 temperatures [106], high metal doses [105] or (iii) with microbial processes [108] or operating  
289 under particular conditions.

290 It is interesting to note that  $\text{Al}^0$  and  $\text{Zn}^0$  could not induce  $\text{ClO}_4^-$  reduction. The extent of  $\text{ClO}_4^-$   
291 removal certainly depends on the operational condition (metal particle size, metal dose,  
292 mixing intensity...) but the qualitative absence of reduction suggests that elemental metal  
293 ( $\text{M}^0$ ) is not basically involved in the process of contaminant reduction in  $\text{M}^0/\text{H}_2\text{O}$  systems.  
294 Accordingly, in  $\text{Fe}^0/\text{H}_2\text{O}$  systems, contaminant reduction is coupled with the complex  
295 processes occurring within the oxide scale on  $\text{Fe}^0$  and the reducing agents are (adsorbed) H  
296 and  $\text{Fe}^{\text{II}}$  species. A proper consideration of the thermodynamics of processes occurring in the  
297 oxide scale on  $\text{Fe}^0$  and the spatial disposition of  $\text{Fe}^0$  and the oxide scale has yielded the same  
298 conclusion [28,29,41,42]. The view that contaminants are quantitatively removed by in-situ  
299 generated corrosion products and reduction occurs in the body of the oxide scale is validated  
300 by the approach comparing  $\text{Fe}^0$  with  $\text{Al}^0$  and  $\text{Zn}^0$  for  $\text{ClO}_4^-$  removal.

### 301 **5 Toxicity of tested elements**

302 Aluminium, iron and zinc are 3 potential toxic metals for animal, humans, micro-organisms  
303 and plants. Accordingly, their toxicity must be discussed before their generalized use in  
304 environmental remediation strategies. Due to their natural abundance, aluminium and iron  
305 may be considered harmless for the environment at first glance. However, the use of each of  
306 the 3 elements must be individually considered at any specific site.

307 The prediction of metal toxicity by evaluation of the relationships between general metal  
308 properties and toxic effects has been a matter of intensive research. Relevant metal toxicity  
309 data included exposure times, organisms, effects and effect levels. Commonly used metal  
310 properties included the oxidation state (OX), the electrochemical potential ( $E^0$ ), the ionization  
311 potential (IP), the atomic radius (AR), the ionic radius (IR), the atomic weight (AW), the  
312 electronegativity ( $X_m$ ) and the atomic number (AN) (Tab. 4). Using these parameters and  
313 revisiting 30 relevant publications, Wolterbeek and Verburg [109] suggested that toxicity  
314 prediction may be performed on basis of selected metal properties without any adoption to  
315 specific organisms, without any division of metals into classes, or grouping of toxicity tests.  
316 The data of Wolterbeek and Verburg [109] suggest that iron and zinc are very similar in their  
317 general toxicity and are both more toxic than aluminium. This trend is not confirmed by the  
318 element permissible limits of World Health Organization maximum for drinking water  
319 (MCL). The MCL values suggest that Al is the most toxic elements while Zn is the less toxic  
320 one, however, it should be highlighted that for iron, the MCL is based on taste issues. In all  
321 the cases, the toxicity to be discussed here concerns all organisms likely to be present in the  
322 environment where a remediation metal/H<sub>2</sub>O system will be installed. Clearly, beside  
323 chemical reactivity for long term contaminant removal, the effect of individual metals on the  
324 environment must be profoundly understood. However, even for iron (including nano-Fe<sup>0</sup>)  
325 comprehensive studies are still lacking [15,17].

## 326 **6 Concluding remarks**

327 This study clearly delineates the synergetic importance of (i) the thermodynamics of iron  
328 oxidative dissolution, (ii) the thermodynamics of Fe oxides precipitation, and (iii) the kinetics  
329 of oxide scale growth (thus its porosity) for the process of contaminant removal in Fe<sup>0</sup>/H<sub>2</sub>O  
330 systems. The comparison with Al<sup>0</sup>/H<sub>2</sub>O and Zn<sup>0</sup>/H<sub>2</sub>O systems has shown that contaminant  
331 reductive transformation results from complex processes taking place within the oxide scale  
332 [34,47]. These processes involved secondary reducing agents (H, H<sub>2</sub> and Fe<sup>II</sup>) possibly

333 adsorbed to the surface of in situ generated minerals. The contribution of electrons from  $\text{Fe}^0$   
334 (direct reduction) for contaminant reduction is not significant.

335 In demonstrating that  $\text{Fe}^0$  is not a significant electron source for contaminant reductive  
336 transformation, this study conciliates two decades of intensive research on remediation with  
337  $\text{Fe}^0$  with almost two centuries aqueous metal corrosion research [47,72,73,77,110-114]. In  
338 fact, eighteen years ago, Stratmann and Müller [115] demonstrated that, in a  $\text{Fe}^0/\text{H}_2\text{O}$  system,  
339  $\text{Fe}^0$  is oxidized by water and molecular  $\text{O}_2$  is reduced by  $\text{Fe}^{\text{II}}$  (from  $\text{Fe}^0$  oxidation). Similarly,  
340 Odziemkowski et al. [65], Lavine et al. [66], Jiao et al. [39] and Ghauch et al. [43-45] could  
341 not identify any significant contribution of direct reduction (electrons from  $\text{Fe}^0$ ) in the  
342 reduction process of several contaminants. On the other hand, the crucial role of corrosion  
343 products in the process of contaminant reduction has been demonstrated [39,46, 116-120].

344 The roles of iron hydroxides/oxides have been belittled by the thermodynamic founded  
345 premise that  $\text{Fe}^0$  is a reducing agent. However, this widely accepted premise has not properly  
346 considered the thermodynamics of: (i) the oxide scale formation, and (ii) the adhesion of  
347 oxide scale to the  $\text{Fe}^0$  surface. In other words, existing models developed to simulate complex  
348 geochemical and physical processes that occur in  $\text{Fe}^0/\text{H}_2\text{O}$  systems [8,121-127] have not  
349 properly considered two important thermodynamic issues. The fact that these models were  
350 reported successful in representing results of laboratory and field tests [13,124-127] questions  
351 the validity of models to predict long-term performance of  $\text{Fe}^0/\text{H}_2\text{O}$  systems. Accordingly,  
352 more reliable models should take into account the evolution of the oxide scale on  $\text{Fe}^0$  over  
353 time. For this enterprise to be successful, more time should be devoted to gain reliable data in  
354 long-term laboratory experiments under relevant conditions. Only such data could enable the  
355 ascertainment of reliable parameters to be incorporated in sound models.

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### 361 **Appendix: Al<sup>0</sup> and Zn<sup>0</sup> for environmental remediation: state-of-the-art**

362 For the sake of completeness, the state-of-the-art knowledge on the process of aqueous  
363 contaminant removal by Al<sup>0</sup> and Zn<sup>0</sup> is succinctly given here.

#### 364 **A.1 Al<sup>0</sup> for environmental remediation**

365 Because of the similitude in crystal structure between Al<sup>0</sup> and Al<sub>2</sub>O<sub>3</sub> [98], Al<sup>0</sup> is rapidly  
366 covered by an impervious Al<sub>2</sub>O<sub>3</sub>-scale rendering Al<sup>0</sup> not suitable for environmental  
367 remediation. Fig. 1 has recalled that Al(OH)<sub>3</sub> is very low soluble. Accordingly, reductive  
368 transformations reported for some contaminants like chlorinated organic compounds [128-  
369 130] were necessarily observed at the beginning of the experiments or under conditions  
370 disturbing the formation of the oxide scale on Al<sup>0</sup>.

371 Bojic et al. [51,131-133] have presented a micro-alloyed aluminium composite (MAIC) as an  
372 attractive medium for aqueous contaminant removal by spontaneous reduction-coagulation  
373 process. Removal by MALC is attractive in terms of both removal efficiency and cost  
374 effectiveness. The MAIC consists of micro-alloyed aluminium coated over a thin iron net  
375 [132]. Its mechanism of action is based on the several physico-chemical processes and the in  
376 situ formation of the coagulant, due to its spontaneous reaction with water. The major  
377 processes are adsorption, reduction, hydrogenation, hydrolysis and coagulation, operating  
378 synergistically to degrade and remove variety of pollutants from water [51]. An examination  
379 of processes occurring in the MAIC treatment shows that Al(OH)<sub>3</sub> flocks act as adsorbents  
380 and/or traps for ions, molecules or suspended particles thus, removing them from the solution  
381 by sorption, co-precipitation or electrostatic attraction followed by coagulation [51]. This  
382 global removal mechanism is the one by which Fe<sup>0</sup>/H<sub>2</sub>O systems operate. In other words,  
383 micro-alloying Al enables the formation of a porous oxide layer on Al<sup>0</sup>. A porous oxide layer  
384 is permeable for ions because of the many defects in the crystal lattice due to different

385 dimensions and charges of micro-alloyed elements, related to  $\text{Al}^{3+}$ . Keeping in mind, that  
386 similar  $\text{Fe}^0$  composites are responsible for the long-term efficiency of SONO arsenic filters  
387 [134,135] the synthesis of several  $\text{Fe}^0$  composites containing various amounts of S (and P)  
388 should be regarded as next generation  $\text{Fe}^0$  media for site specific applications. Remember that  
389 S (and P) is an undesirable alloying element in the steel and iron production because of its  
390 ability to form high reactive electrochemical cells acceleration corrosion.

## 391 **A.2 $\text{Zn}^0$ for environmental remediation**

392  $\text{Zn}^0$  has been presented as an attractive alternative to  $\text{Fe}^0$  for environmental remediation [48-  
393 50,54-56,100,136-142]. This is mostly due to the relative high solubility of zinc-bearing  
394 minerals compared to iron-bearing minerals [143]. Accordingly,  $\text{Zn}^0$  can maintain its  
395 reactivity for a longer period of time than  $\text{Fe}^0$ . Fig. 1 corroborates these findings as  $\text{Zn}^{\text{II}}$  is  
396 essentially more soluble than  $\text{Fe}^{\text{III}}$ . Remember, the oxidation of  $\text{Fe}^{\text{II}}$  to  $\text{Fe}^{\text{III}}$  occurs even under  
397 strong anoxic conditions and that the solubility of polymerised  $\text{Fe}^{\text{II}}$  is by far lower than that of  
398 hydrated  $\text{Fe}^{\text{II}}$  [97]. The higher reactivity of  $\text{Zn}^0$  is necessarily coupled with high  $\text{Zn}^{\text{II}}$   
399 concentration. However, effort to monitor and control toxic generated  $\text{Zn}^{\text{II}}$  are recent. For  
400 example Song et al. [143] positively tested the possibility of using hydroxyapatite in  
401 combination with  $\text{Zn}^0$  to control  $\text{Zn}^{\text{II}}$  concentration. In other words, in comparison to  $\text{Fe}^0$ , the  
402 increased reactivity of  $\text{Zn}^0$  is coupled with high  $\text{Zn}^{\text{II}}$  concentrations in effluents. Reports on  
403 Zn-composites similar to MAIC from Bojic et al. [51,131-133] were not found.

404

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- 752

752 **Figure captions**

753

754 **Figure 1:** pH dependence of metal hydroxide solubility. A clear pH-dependence of hydroxide  
755 solubility can be observed. Considered minerals are  $\text{Al(OH)}_3$ ,  $\text{Fe(OH)}_2$ ,  $\text{Fe(OH)}_3$  and  
756  $\text{Zn(OH)}_2$ .

757

757 **Table 1:** Standard electrode potentials of water constituents ( $H^+$ ,  $O_2$ ) and relevant redox  
758 couples for  $Al^0/H_2O$  ( $Al^{III}/Al^0$ ),  $Fe^0/H_2O$  ( $Fe^{II}/Fe^0$  and  $Fe^{III}/Fe^{II}$ ), and  $Zn^0/H_2O$   
759 ( $Zn^{II}/Zn^0$ ) systems.  $E^0$  are arranged in increasing order. The lower the  $E^0$  value, the stronger  
760 the reducing capacity of  $Al^0$  ( $Fe^0$  or  $Zn^0$ ) for the oxidant of a couple. Note that  $Al^{3+}$  can not be  
761 reduced in  $Fe^0/H_2O$  systems whereas  $Fe^{2+}$  is reduced in  $Al^0/H_2O$  and  $Zn^0/H_2O$  systems.  $E^0$   
762 values are from Gerasimov et al. [79].

763

Reaction		$E^0$ (V)	Eq.
$Al^0$	$\Leftrightarrow$	$Al^{3+} + 3 e^-$	-1.66 (3)
$Zn^0$	$\Leftrightarrow$	$Zn^{2+} + 2 e^-$	-0.76 (4)
$Fe^0$	$\Leftrightarrow$	$Fe^{2+} + 2 e^-$	-0.44 (5)
$Fe^{2+}_{(s)}$	$\Leftrightarrow$	$Fe^{3+}_{(s)} + e^-$	-0.36 to -0.65 (6)
$H^+ + e^-$	$\Leftrightarrow$	$\frac{1}{2} H_2 (g)$	0.00 (7)
$Fe^{2+}$	$\Leftrightarrow$	$Fe^{3+} + e^-$	0.77 (8)
$O_2 + 2 H_2O + 4 e^-$	$\Leftrightarrow$	$4 OH^-$	0.81 (9)

764

765



765 **Table 2:** Solubility of metal hydroxides relevant for the discussion in this study at pH 7. Data  
 766 from Lewis [96].

767

Reaction			$K_s$	Eq.
$Al^{3+} + 3 OH^{-}$	$\Leftrightarrow$	$Al(OH)_3$	$10^{-8.1}$	(12)
$Al(OH)_3$	$\Rightarrow$	$Al_2O_3$		(12a)
$Fe^{2+} + 2 OH^{-}$	$\Leftrightarrow$	$Fe(OH)_2$	$10^{0.16}$	(13)
$Fe^{3+} + 3 OH^{-}$	$\Leftrightarrow$	$Fe(OH)_3$	$10^{-7.5}$	(14)
$Fe(OH)_2, Fe(OH)_3$	$\Rightarrow$	$FeOOH, Fe_2O_3, Fe_3O_4$		(13a, 14a)
$Zn^{2+} + 2 OH^{-}$	$\Leftrightarrow$	$Zn(OH)_2$	$10^{-1.1}$	(15)
$Zn(OH)_2$	$\Rightarrow$	$ZnO$		(15a)

768

769

769 **Table 3:** Experimental conditions and mechanism of  $\text{ClO}_4^-$  removal in selected  $\text{Al}^0/\text{H}_2\text{O}$ ,  
 770  $\text{Al}/\text{Fe}^0/\text{H}_2\text{O}$ ,  $\text{Fe}^0/\text{H}_2\text{O}$  and  $\text{Zn}^0/\text{H}_2\text{O}$  systems. It is evident that  $\text{ClO}_4^-$  reduction occurs only in  
 771  $\text{Fe}^0$ -bearing systems.

772

<b>Medium</b>	<b>loading</b>	<b>Mixing</b>	<b>concentration</b>	<b>pH</b>	<b>time</b>	<b>Mechanism</b>	<b>Reference</b>
	( $\text{gL}^{-1}$ )	( $\text{min}^{-1}$ )	( $\text{mgL}^{-1}$ )		(h)		
Al	5 to 35	180	10.0	5.2	24	Adsorption	[85]
Fe	400	20	10.2	7.0	336	Partial reduction	[105]
Fe	1000	shaken	1.0	5.0	300	Partial reduction	[82]
Zn	1000	shaken	1.0	5.0	300	No removal	[82]

773

774

775

775 **Table 4:** Characteristic parameters (OX,  $E^0$ , IP, X<sub>m</sub>, AR, IR, AW, and AN) of metals relevant  
 776 for toxicity evaluation, WHO element maximum permissible limits in drinking water (MCL),  
 777 and averaged order numbers of toxicity relative to 80 metal ions after Wolterbeek and  
 778 Verburg [109]. The relative toxicity values are given together with the uncertainties in the  
 779 respective positions. A toxicity value of 80 corresponds to the most toxic element and a value  
 780 of 1 to the least toxic.

781

<b>X</b>	<b>OX</b>	<b>E<sup>0</sup></b>	<b>IP</b>	<b>X<sub>m</sub></b>	<b>AR</b>	<b>IR</b>	<b>AW</b>	<b>AN</b>	<b>MCL</b>	<b>Toxicity</b>
	(-)	(V)	(-)	(-)	(Å)	(Å)	(g <sub>mol</sub> <sup>-1</sup> )	(-)	(ppm)	(-)
<b>Al</b>	3	1.662	28.45	1.61	0.54	0.54	26.98	13	0.2	15.1 ± 10.4
<b>Fe</b>	2	0.447	16.19	1.83	1.24	0.61	55.84	26	0.3	36.4 ± 11.5
<b>Fe</b>	3	0.771	30.65	1.83	1.24	0.55	55.84	26	0.3	29.8 ± 9.5
<b>Zn</b>	2	0.762	17.96	1.81	1.31	0.74	65.37	30	5.0	35.6 ± 6.5

782 X = Element, OX = Oxidation state,  $E^0$  = electrochemical potential, IP = ionization potential, X<sub>m</sub> =  
 783 electronegativity, AR = atomic radius, IR = ionic radius, AW = atomic weight, AN = atomic number.

784

785