1   **On the suitability of admixing sand to metallic iron for water treatment**

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7

8   **Abstract**

9   This communication clarifies the relationships between sand addition and the sustainability of

10   iron/water systems for environmental remediation. It is shown that any enhanced contaminant

11   removal in an iron/sand/water relative to an iron/water system is related to the

12   avoidance/delay of particle cementation by virtue of the inert nature of sand. The argument

13   that sand dissolution produces protons (H^+) to sustain iron corrosion is disproved by the very

14   low dissolution kinetics solubility of SiO_2-bearing minerals under environmental conditions.

15   This demonstration corroborates the concept that aqueous contaminant removal in iron/water

16   systems is not a process mediated by electrons from Fe^0.

17

18   **Keywords:** Adsorption, Co-precipitation, Dissolution kinetics, Sand admixture, Zerovalent

19   iron.

20

1.   Introduction

The use of metallic iron (Fe^0) has become an established technology for environmental remediation and water treatment in recent years (O´Hannesin and Gillham, 1998; Odziemkowski and Simpraga, 2004; Bartzas et al., 2006; Li et al., 2006; Henderson and Demond, 2007; Hussam and Munir, 2007; Hussam, 2009; Noubactep et al. 2009a; O et al., 2009; Bartzas and Komnitsas, 2010; Li and Benson, 2010; Comba et al., 2011; Gheju, 2011; Gunawardana et al., 2011; Jeen et al., 2011; Allred, 2012; Ingram et al., 2012; Jeen et al., 2012; Huang et al., 2012; Noubactep et al., 2012a; Ruhl et al., 2012a; Ruhl et al., 2012b; Ruhl et al., 2012c). The processes governing contaminant removal are considered widely understood (Cong et al., 2010; Henderson and Demond, 2011; ITRC, 2011; Chen et al. 2012a; Jeen et al., 2012; Huang et al., 2013a; Huang et al., 2013b). Meanwhile, reported studies are focused on ways to enhance the Fe^0 reactivity such as using nano-sized particles and bimetallic systems (Ghauch et al., 2011; Crane and Scott, 2012; Noubactep et al., 2012a), using other reactive metallic elements (e.g. Al^0, Ti^0, Zn^0) (Bojic et al., 2007; Sarathy et al., 2010; Guo et al., 2012; Lee et al., 2012; Salter-Blanc et al., 2012) or using hybridized systems like $Fe^0/Fe_3O_4/Fe^{II}$ (Huang et al., 2012; Huang et al., 2013a; Huang et al., 2013b). However, the validity of the current paradigm has been seriously questioned as the relevance of direct reduction (reduction by electrons from Fe^0) for observed efficiency of Fe^0/H_2O systems was challenged (Lavine et al., 2001; Noubactep, 2007; Noubactep, 2008; Jiao et al., 2009; Ghauch et al., 2010; Noubactep, 2010a; Noubactep, 2010b; Ghauch et al., 2011; Gheju and Balcu 2011; Noubactep, 2011a; Noubactep, 2011b; Noubactep, 2012a; Liu et al., 2013). The problem is well worthy to be discussed further. The present contribution focuses on the use of sand as additive material in Fe^0 filtration systems.

The idea that sand/quartz (SiO_2) admixture enhances the extent/efficiency of contaminant removal in Fe^0/H_2O systems has significant support in the literature (Powell et al., 1995; Kaplan and Gilmore, 2004; Song et al., 2005; Wu et al., 2005; Guo et al., 2011). This idea co-

46   exists with concerns that SiO_2 addition is a 'dilution' of reactive materials and is necessarily

47   accompanied by slower kinetics and lower extent of the decontamination process (Devlin and

48   Patchen, 2004; Bi et al., 2009; Ruhl et al. 2012a). Each of this argument is seemingly

49   supported by strong experimental evidence and has let to the recent statement that "there is no

50   conclusive evidence that a sand/iron mix is better or worse than a pure iron barrier" (Ulsamer,

51   2011). Moreover, although the efficiency of Fe^0 PRBs was demonstrated with a 22:78

52   Fe^0:sand w/w mixture for the removal of TCE (O´Hannesin and Gillham, 1998), Ruhl et al.

53   (2012a) recently demonstrated the inefficiency of dual Fe:additive mixtures for the removal of

54   the same compound (e.g. TCE) from a contaminated groundwater. Tested additives included

55   anthracite, gravel, pumice and sand.

56   The objective of this paper is to clarify the impact of sand addition on the long term efficiency

57   (or sustainability) of Fe^0/H_2O systems using a mathematical modelling. The discussion starts

58   by a careful analysis of the $Fe^0/sand/H_2O$ system on a pure chemical perspective.

## 59   2.   The chemistry of the $Fe^0/sand/H_2O$ system

60   The presentation in this section is limited to an ideal anoxic system (absence of oxygen).

61   Under such conditions Fe^0 is oxidized by protons (H^+) from water dissociation after Eq. 1:

62    $$Fe^0 + 2 H^+ \Rightarrow Fe^{2+} + H_2 \qquad\qquad (1)$$
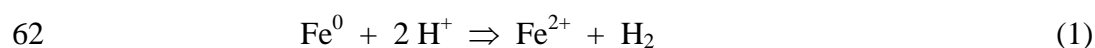
63   After the Lechatelier's Principle, Eq. 1 is sustained/enhanced in a system if: (i) H^+ is

64   produced, (ii) Fe^{2+} is consumed and (iii) H_2 is consumed or escapes out of the system.

65   Is the view that sand sustains the efficiency of Fe^0 supported by Lechatelier's Principle? It is

66   obvious that sand is not a reservoir of H_2. Accordingly, H_2 may escape or be used for

67   microbial activities. Sand may potentially adsorb Fe^{2+} but its adsorption capacity is limited

68   and any redox reaction of adsorbed Fe^{II}-species is only indirectly coupled with the parent Fe^0.

69   The last discussed option is that sand may produced protons. The ability of sand to produce

70   protons has been documented in the Fe^0 literature (Powell et al., 1995; Blowes et al., 1997;

71   Powell and Puls, 1997). In this context a 'buffering effect' of SiO_2-bearing materials has been

reported. However, because of the very slow rate of SiO_2 dissolution (Rimstidt and Barnes, 1980; Kehew, 2001), it is doubtful whether any significant acidification by SiO_2 dissolution may occur (Eq. 2). The observed pH decrease in short-term batch experiments can be attributed to hydrodynamic effects (mixing operations) dissolving weathered fines from the surface of used materials. After this initial dissolution observed in Batch experiments, no quantitative SiO_2 dissolution could be expected at pH $\geq$ 4.5.

$$SiO_{2(s)} + 2\,H_2O \Rightarrow H_4SiO_4(aq) \tag{2}$$
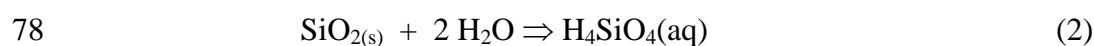
The presentation until now shows that sand admixture can not actively sustain the efficiency of Fe^0/H_2O systems in the long-term. Therefore, the observed enhanced efficiency (Song et al., 2005; Bi et al., 2009; Gottinger et al., 2010) should be explained by other processes.

3.   The operating mode of Fe^0/sand/H_2O

3.1   Descriptive aspects

Sand is a geo-material conventionally used for water treatment (Darcy, 1856; Weber-Shirk and Dick, 1997; Ngai et al., 2007; Kubare and Haarhoff, 2010; Gottinger et al., 2011). Sand is mostly considered a non reactive material for media filtration. In some cases, this material is mixed with reactive natural materials to sustain selective removal of some species (Yao et al., 1971; Ali, 2012). Tested natural reactive materials include iron ores (e.g. siderite, hematite), manganese ores, volcanic stones, and zeolites (Guo et al., 2007a; Guo et al., 2007b; Doula, 2009). In other cases, sand is artificially coated with reactive media such as iron or manganese oxides (Gupta et al., 2005). While filtration on pure sand bed is termed 'media filtration' (size-exclusion of suspended particles), adsorption on coated sand is known as 'adsorptive filtration' (Edwards and Benjamin, 1989; Dermatas and Meng, 2004). This classification is operational as sand may adsorb some species more strongly than iron oxides. A classical example was reported by Mitchell et al. (1955). These authors demonstrates that some iron oxide coated sands are worse adsorbents for methylene blue than original materials (non-coated). The observation of Mitchell et al. (1955) is very important for the design of Fe^0

98   filtration systems. In fact, species that are not readily removed by iron oxide coated sand

99   should be removed before the Fe^0-containing zone, for instance on a granular carbon or sand

100   layers. For the purpose of this communication it is sufficient to consider that in a

101   Fe^0/sand/H_2O system, iron-oxide-coated sand is generated in-situ.

102   Previous theoretical studies have argued that a Fe^0-containing zone must be situated after one

103   or several biosand filters to operate under anoxic conditions where less expansive corrosion

104   products are generated (Noubactep et al., 2009a; Noubactep, 2010c; Noubactep and Caré,

105   2010; Noubactep and Schöner, 2010; Noubactep et al., 2010; Noubactep et al. 2012b;

106   Noubactep et al. 2012c). Methylene blue can be regarded as proxies for all species with low

107   adsorptive affinity to iron oxides. This observation of Mitchell et al. (1955) corroborates the

108   view that, in a multi-barriers system, a Fe^0-containing zone must never be implemented at the

109   beginning of the chain. Moreover, the fact that methylene blue is quantitatively removed in

110   Fe^0/sand systems (Noubactep, 2009; Chen et al., 2012b; Miyajima and Noubactep, 2012;

111   Btatkeu et al., 2013; Miyajima and Noubactep, 2013) confirms that adsorption, co-

112   precipitation and enhanced size-exclusion are the fundamental mechanisms of contaminant

113   removal in Fe^0/H_2O systems. Accordingly, despite the low affinity of MB for adsorbing

114   species in Fe^0/H_2O systems, quantitative MB removal can be achieved upon proper system

115   design (Btatkeu et al., 2013). Recent calculations have demonstrated that using the same mass

116   of Fe^0, the best treatment system is achieved in using the column with the smallest diameter

117   (Noubactep et al. 2012c). In such beds/columns Fe^0 is mixed with a non expansive material,

118   e.g. sand. The most favourable Fe^0 volumetric proportions are bellow 50 % (Miyajima, 2012;

119   Miyajima and Noubactep, 2013), but the intrinsic reactivity of Fe^0 and the relative geometry

120   of Fe^0 and sand should be considered as well (O et al., 2009; Caré et al. 2012, Btatkeu et al.

121   2013). It is hoped that all these aspects will be considered in future system design.

122   ***3.2   Sand as dispersant***

123 Aqueous iron corrosion at pH > 4.5 is a cycle of (i) oxidative dissolution ($Fe^0 \Rightarrow Fe^{2+}$), (ii)

124 solvatation ($Fe(H_2O)_6^{2+}$), (iii) volumetric expansion (formation of $Fe(OH)_n$ colloids), (iv)

125 volumetric contraction (Fe hydroxides/oxides) processes. The overall process is known as

126 'volumetric expansion' (Noubactep, 2010c; Noubactep and Schöner, 2010; Noubactep,

127 2011c). The volume of any iron Fe hydroxide or oxide is higher than that of the original metal

128 (Fe^0) (Pilling and Bedworth, 1923; Caré et al., 2008). The ratio between the volume of

129 expansive corrosion product and the volume of iron consumed in the corrosion process is

130 called ''rust expansion coefficient''. However, this coefficient does not reflect the

131 intermediary expansive stage of the process which yield volumetric colloids that are capable

132 of enmeshing foreign species during their further transformation to oxides (Noubactep, 2010a;

133 2010c; 2011c, 2012a). More importantly, these volumetric colloids have the ability to

134 'cement' or 'compact' granular particles (Mackenzie et al., 1999; Kaplan and Gilmore, 2004).

135 The cementation process results in limited access to all three potential removing agents: non

136 corroded Fe^0, iron oxides and sand. Thus contaminant removal by adsorption and/or co-

137 precipitation is inhibited. On the contrary, in fest bed filtration systems, adsorptive size-

138 exclusion is enhanced but the system permeability is reduced (permeability loss). This is the

139 first reason why pure Fe^0 systems (100 % Fe^0) are efficient but not sustainable (Hussam,

140 2009; Noubactep et al., 2010).

141 Regarding Fe^0 particles as 'cement generators' suggests that the first tool to limit

142 cementation/compaction is to decrease the proportion of Fe^0 (Caré et al., 2012; Noubactep et

143 al., 2012b). In other words, batch and column systems with 100 % Fe^0 leave no room for solid

144 phase expansion (Miyajima and Noubactep, 2012). Such systems will 'clog' rapidly and iron

145 corrosion and the corresponding contaminant removal will be minimal. In other words, sand

146 and other non expansive additives should not be regarded as material slowing the mass

147 transport of reactants to the Fe^0 surface but rather as a dispersant sustaining the system's

148 efficiency (more Fe^0 is consumed, more adsorbing agents are produced) (Noubactep et al.,

149 2012b). The use of non-reactive materials to sustain Fe^0 efficiency is current at nano-scale

150 (Gheju, 2011; ITRC, 2011; Crane and Scott, 2012; Noubactep et al., 2012a). On the other

151 hand, the efficiency of the hybridized $Fe^0/Fe_3O_4/Fe^{II}$ presented by Huang et al. (2012; 2013a;

152 2013b) can be attributed to the non/less expansive nature of Fe_3O_4 (magnetite) and the

153 enhanced reactivity of Fe^{II} adsorbed onto magnetite and nascent iron hydroxides (Charlet et

154 al., 1998; Liger et al., 1999; Noubactep, 2007; Noubactep, 2008; Noubactep, 2011a).

155 Regarding sand and other non-expansive additives as useful tools to sustain Fe^0 efficiency

156 explains all reported discrepancies on the effect of sand addition on the efficiency of Fe^0/H_2O

157 systems. In particular, the statement of Ulsamer (2011) that "there is no conclusive evidence

158 that a sand/iron mix is better or worse than a pure iron barrier" is due to the fact that results

159 have been compared with little care on the operational conditions of their production (Crane

160 and Noubactep, 2012; Noubactep, 2012b). Additionally, there is still no index to characterize

161 the intrinsic reactivity of Fe^0 material (Noubactep et al., 2009b; Miyajima and Noubactep,

162 2012; Btatkeu et al., 2013; Miyajima and Noubactep, 2013). For example, a filtration system

163 (e.g. a column) containing 100 % of a less reactive material (material A) may not experience

164 clogging while a readily reactive material (material B) could induce clogging even at 40 %

165 volumetric proportion within similar working conditions. In other words, the suitability of

166 admixing additive to iron can not be accessed before the intrinsic reactivity is properly

167 characterized. Beside the Fe^0 intrinsic reactivity, other relevant factors influencing the

168 porosity of filtration beds should be considered (Kubare and Haarhoff, 2010; Caré et al.,

169 2012; Btatkeu et al., 2013; Miyajima and Noubactep, 2013). Factors influencing the

170 efficiency of Fe^0 filtration systems include: (i) the particle size and form of reactive materials,

171 (ii) the dimensions of the treatment systems and (ii) the chemistry of raw waters (Noubactep

172 et al., 2012c; Caré et al., 2012; Crane and Noubactep, 2012; Ruhl et al., 2012b; Togue-Kamga

173 et al., 2012a, Togue-Kamga et al., 2012b; Btatkeu et al., 2013; Miyajima and Noubactep,

174 2013).

4. Discussing the process of permeability loss in Fe^0/H_2O systems

In this section, an evaluation of permeability loss in a series of filters (e.g. reactive zones) with an initial pore volume $V_p = 100$ mL is given. Assuming an initial porosity of 40 % the volume of the filter is $V_{rz} = 250$ mL and the volume of solid is $V_{solid} = 150$ mL. This volume can be occupied by 1170 g of granular Fe^0 (density: 7.8 g/cm^3). It is assumed that this filter is used to (electro)chemically reduce CrO_7^{2-} to Cr^{3+} (Eq. 1) which is then precipitated as Cr_2O_3 (unit cell volume: 289.85 A$^{\circ 3}$ corresponding to 174.6 mL/mol) (Prewitt et al., 1969) under anoxic conditions (Fe_3O_4 is the major iron corrosion product).

$$3\ Fe^0\ +\ Cr_2O_7^{2-}\ +\ 14\ H^+\ \Rightarrow 3\ Fe^{2+}\ +\ 2\ Cr^{3+}\ +\ 7\ H_2O \qquad (1)$$
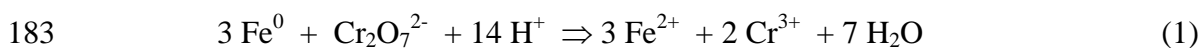
The initial pore volume ($V_p = 100$ mL) is completely filled when 570 g of Fe^0 (10.17 moles) is oxidized and precipitated as Fe_3O_4. Accordingly, using a 100 % Fe^0 bed corresponds to a 51.3 % material wastage with the additional disadvantage that the system is not sustainable. Assuming that Fe^0 oxidation is coupled to chemical Cr^{VI} reduction (Eq. 1), the initial pore volume is filled by only 0.57 mole of Cr_2O_3. This corresponds to the oxidation of 1.72 moles of Fe^0 (by 0.57 mole of $Cr_2O_7^{2-}$). 0.57 mole is contained in 29,640 L of a 1 mg/L $Cr_2O_7^{2-}$. In other words, up to 30 m^3 of water containing 1 mg/L $Cr_2O_7^{2-}$ can be treated by only 600 g (0.6 kg) of Fe^0. These calculations corroborate the huge potential of Fe^0/H_2O systems for water treatment while disapproving the current expression of the removal capacity (in mg contaminant per g Fe^0) partly derived from batch experiments.

Summarized, $V_p = 100$ mL is completely clogged when (i) 10.17 moles of Fe^0 is oxidized by water and subsequently precipitated as Fe_3O_4 or (ii) 1.72 moles of Fe^0 is oxidized by 0.57 mole $Cr_2O_7^{2-}$ to form 0.57 mole of Cr_2O_3. However, it should be kept in mind that $Cr_2O_7^{2-}$ can be removed without reduction and corrosion products are always oxides/hydroxides mixtures.

4.1 Permeability loss resulting from expansive corrosion

The methodology for the assessment of the permeability loss is explicitly presented in Caré et al. (2012). Fe^0/sand systems with Fe^0 volumetric ratios (τ_{ZVI}) varying from 0 to 100 % are

201 considered. A Fe^0 filter is made up of granular solid materials (Fe^0, sand) and the voids

202 between the grains (pore volume, V_p). The volume of the reactive zone is given by (Eq. 2):

203 $$V_{rz} = V_{ZVI} + V_{sand} + V_p \qquad (2)$$

204 Ideally, a reactive zone is clogged when V_p is completely filled with retained solutes,

205 suspended particles and/or in-situ generated species. However, clogging is usually observed

206 only at the entrance zone of Fe^0 systems (Mackenzie et al., 1999; Kaplan and Gilmore, 2004;

207 O et al., 2009).

208 Upon oxidative dissolution and subsequent precipitation, the volume of each corrosion

209 product (e.g. Fe_3O_4; $\eta = 2.08$) is higher than that of the original metal (Pilling and Bedworth,

210 1923). The excess volume contributing to system clogging is given by V_{excess} in Eq. 3 (Caré et

211 al., 2012).

212 $$(\eta - 1) * \tau_{ZVI} * V_{solid} = V_{excess} \qquad (3)$$

213 Where τ_{ZVI} ($0 \leq \tau_{ZVI} \leq 1$) is the volumetric fraction of metallic iron relative to the solid phase

214 in the bed or the reactive layer.

215 The Fe^0 filtration system is clogged when the volume V_{excess} is equal to the initial inter-

216 granular voids (V_p).

217 $$(\eta - 1) * \tau_{ZVI} * V_{solid} = V_p \qquad (3a)$$

218 Eq. 4 suggests that, for every η value (i.e. every oxide), V_p is a linear function of τ_{ZVI} (Fig. 1).

219 Negative values of V_p are not considered as they have no physical meaning. In other words,

220 $V_p < 0$ indicates an excess of Fe^0 and system clogging occurred before complete Fe^0

221 depletion.

222 *4.2   Contaminant accumulation and permeability loss*

223 The calculations in this work consider solely the initial state (Fe^0) and the final state (Fe_3O_4).

224 The kinetics of the corrosion reaction is difficult to access. In the oil industry, the corrosion

225 rates of external line pipe are expected to be < 10 μmyr^{-1} but could increase to up to 700

226 μmyr^{-1} in the presence of sulfate reducing bacteria (Sherar et al., 2011). In the Fe^0 remediation

227 industry, no such experience-based guide values have been published. The paramount factors

228 determining the corrosion kinetics include: (i) the intrinsic reactivity of Fe^0 materials, (ii) the

229 water chemistry (pH, dissolved O$_2$, nature and extent of contamination) and (iii) water flow

230 rate.

231 In this section, the occupation of the pore volume by removed Cr (as crystalline Cr$_2$O$_3$) is

232 discussed. The evolution of a system initially containing 50 % Fe^0 (τ_{ZVI} = 0.5) is characterized

233 as the extent of Fe^0 depletion (α_{ZVI}) varies from 0 to 100 %. It is assumed that corrosion

234 products results solely from Fe^0 oxidation by Cr^{VI} (Fe^0:Cr^{III} = 3:2 or Fe^0:Cr$_2$O$_3$ = 3:1).

235 Fig. 2 summarizes the results and shows unambiguously that porosity loss due to pore filling

236 with insi-situ generated corrosion products is significant. While considering the pore

237 occupation by Cr$_2$O$_3$ it is seen that V$_p$ is completely clogged when only 5 % of the initial

238 amount of Fe^0 has reacted with Cr^{VI} to form crystalline Cr$_2$O$_3$. Considering Fe$_3$O$_4$ alone,

239 complete clogging occurred when about 75 % of the initial amount of iron is consumed. This

240 conclusion seem to underscore the impact of iron corrosion products in filling the initial

241 porosity. However, one should remember that water oxidizes Fe^0 and contaminants are

242 present in trace amounts (Henderson and Demond, 2011; Kümmerer, 2011). Iron oxides

243 certainly quantitatively precipitate (at pH > 5.0). In other words, the calculated volume

244 occupation by Fe$_3$O$_4$ is very conservative and even unrealistic because strict stoichoimetric

245 reduction by Fe^0 has never been reported (Gould et al., 1982). In other words, stoichoimetric

246 Cr^{VI} reduction by Fe^0 is unlikely to occur under environmental conditions. Fig. 2 presents the

247 line for a reaction efficiency of 33 % meaning that for 3 moles of dissolved Fe^{2+}, 'only' one

248 mole induces Cr^{VI} reduction. In this case, system clogging is observed just at 20 % Fe^0

249 consumption.

250 The last important issue from Fig. 2 is the representation of the percent consumption of Fe^0.

251 At α_{ZVI} = 0, the system behaves like a pure sand filter. As α_{ZVI} increases, the efficiency of the

252 system virtually increases. Fe^0 corrosion stops when the residual porosity is zero. Fig. 2

253 shows clearly that any Fe^0-amended sand filter, has to find a compromise between (i)

254 increased efficiency by virtue of the Fe^0 reactivity and (ii) reduced porosity as result of

255 expansive iron corrosion. Fig. 2 suggests that for a system containing 50 % (vol/vol) Fe^0, and

256 working under anoxic conditions, this optimum system is around 40 %. Given the difference

257 in density between Fe^0 (7.8 g cm^{-3}) and sand (2.6 g cm^{-3}) the corresponding weight ratio is

258 necessarily lower than 1:1 (50 % w/w) which has been commonly tested and used (Miyajima,

259 2012). In other words, suitable Fe^0/sand systems are yet to be tested. However, it is certain

260 that enhanced contaminant removal in Fe^0/sand/H_2O relative to Fe^0/H_2O systems is related to

261 the delay of particle cementation by virtue of the inert nature of sand.

5.   Concluding remarks

263 Decrease of the hydraulic conductivity (permeability loss) in Fe^0 filtration systems has not

264 been attributed to volumetric expansive iron corrosion. The calculations presented here

265 demonstrate that gas (H_2) evolution and foreign solid precipitation may not be responsible for

266 the majority of permeability loss (Fig. 2). The kinetics and the extent to which permeability

267 loss occurs at a given site depends both on the intrinsic reactivity of used Fe^0 and on the water

268 chemistry. However, it is certain that pure Fe^0 filtration systems are not sustainable as little

269 room is left for iron corrosion (volumetric expansion). Accordingly, any argumentation that

270 sand addition avoid the passivation of the Fe^0 surface or acts as buffering agent thanks to

271 production of silicic acid is faulty. This evidence can only be acknowledged when the whole

272 Fe^0 remediation community has considered the overall theory of the system. Without a theory

273 of the system, new data will be produced but significant advance in knowledge will not be

274 achieved.

275 An essential prerequisite for the universal acceptance of Fe^0 as a remediation technology is a

276 fundamental understanding of processes occurring in Fe^0/H_2O systems. The introduction of

277 this promising technology was based on a false explanation of good experimental

278 observations. The original error was identified and widely presented in the international

279 literature since 2007. The scientific community has not yet dealt with the issue and is

280 presently virtually divided into two schools: pro and contra "reductive transformation" or

281 "adsorption, co-precipitation, size-exclusion". However, the latter concept was clearly

282 presented as a revision of the former. The long-lasting sterile discussion should stop now and

283 efforts should focus on developing the chemistry free Fe^0 technology.

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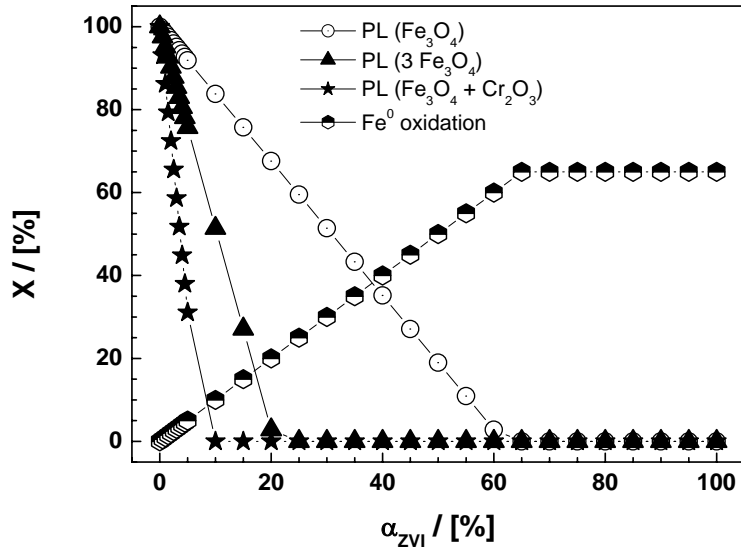
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555 **Figure 1**

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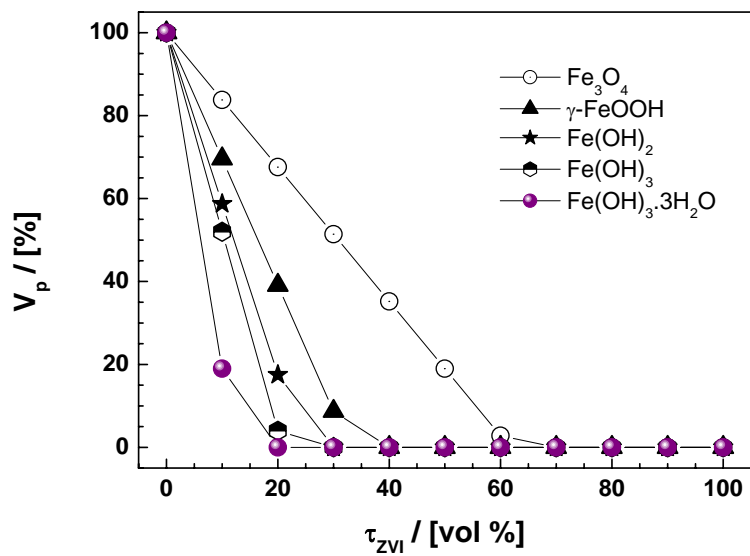
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559   **Figure 2**

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564 **Figure Caption**

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566 **Figure 1:** Evolution of the residual porosity (V_p) as function of the Fe^0 volumetric ratio (τ_{ZVI})

567 in the reactive zone for various iron corrosion products. It is seen that Fe^0 ratios >

568 60 % are pure material wastage. The more sustainable systems are those working

569 under anoxic conditions (Fe_3O_4 as major corrosion product).

570

571 **Figure 2:** Evolution of the porosity loss (PL) and the theoretical extent of iron oxidation as

572 function of the % consumed Fe (α_{ZVI}) in an anoxic system initially containing 50

573 % Fe^0 particles (and 50 % quartz). It is assumed that Fe^0 is oxidized solely by

574 $Cr_2O_7^{2-}$ and produce crystalline Cr_2O_3. PL is due both to pore filling by Cr_2O_3 and

575 Fe_3O_4. In one case an efficiency of 33 % is assumed (3 Fe_3O_4).

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