

1 **Aqueous contaminant removal by metallic iron: Is the paradigm shifting?**

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7 **Abstract**

8 Chemical reduction has long dominated the thinking about the mechanism of aqueous
9 contaminant removal in the presence of metallic iron (e.g. Fe⁰/H₂O systems). However, a
10 large body of experimental evidence indicates that chemical reduction is not adequate to
11 explain satisfactorily the efficiency of Fe⁰/H₂O systems for several substances or classes of
12 substances. By contrast, the alternative approach, that contaminants are fundamentally
13 adsorbed and co-precipitated by iron corrosion products seems to provide a better explanation
14 of observed efficiency. The new approach is obviously not really understood. The present
15 communication aims at clarifying this key issue. It seems that a paradigm shift is necessary
16 for the further development of the iron technology.

17 **Key words:** Contaminant removal, Paradigm shift, Removal mechanism, Water treatment;
18 Zerovalent iron.

19 **1 Introduction**

20 The publication by Thomas Kuhn (1962) of his book “The structure of scientific revolutions”
21 is the starting point of the frequent use of the word “paradigm” in many fields of science.
22 Kuhn characterized a paradigm as a shared theory of the nature of something or of how it
23 operates, together with a related set of problems to be solved and a kit of tools or methods for
24 approaching those problems (Heaney, 2003; Rowbottom, 2011). Researchers introduced into
25 the field, learned about the paradigm. Their challenge is to apply some tools of the prevailing
26 paradigm to clarify some of its unsolved problems. For the field of water treatment with
27 metallic iron (Fe⁰), it is safe to say that contaminant reduction by Fe⁰ constitutes the basis of
28 its operative paradigm.

29 Since the introduction of Fe⁰ for water treatment in 1990 (Reynolds et al., 1990; Gillham and
30 O’Hannesin, 1994), contaminants have been reported to be removed by reductive
31 transformations (Matheson and Tratnyek, 1994; Weber, 1996; O’Hannesin and Gillham,
32 1998; Comba et al., 2011). Clearly, contaminants were considered to be removed because of
33 their chemical transformations possibly making them less harmful (degradation) or less
34 mobile (precipitation). Accordingly, the case for which contaminant reduction products may
35 be more toxic than parent contaminants (e.g. CCl₄) is still actively discussed (Jiao et al., 2009;

36 Alvarado et al., 2010). Moreover, the formation of the universal oxide film on the Fe⁰ surface
37 (reactivity loss) and the pore filling by iron corrosion products (permeability loss) have been
38 regarded as the major inhibitive factors for the process of contaminant removal (Henderson
39 and Demond, 2007; Ghauch, 2008a; Simon et al., 2008; Li and Benson, 2010). Accordingly,
40 three major opened problems of the Fe⁰ technology are: (i) how can harmful reaction products
41 be removed? (ii) how can reactivity loss be prevented? and how can permeability loss be
42 properly considered?

43 Several analytical tools and complicated experimental devices has been used during the past
44 two decades to search for answers to these three questions (Wilderer et al., 2002; McGuire et
45 al., 2003; Simon et al., 2004). Even today, a cursory survey of the literature on Fe⁰ technology
46 will find, in the introduction of virtually every paper, some such phrases as "...Fe⁰ is proved
47 to be particularly suitable for the decontamination of halogenated organic compounds, but
48 subsequent studies have confirmed the possibility of using Fe⁰ for the reduction of nitrate,
49 bromated, chlorate, nitro aromatic compounds, brominated pesticides. Fe⁰ proved to be
50 effective in removing arsenic, lead, uranium and hexavalent chromium..." (Groza et al.,
51 2009). It is important to notice that "contaminant reduction" and "contaminant removal" are
52 mostly randomly interchanged.

53 It should be explicitly stated that some researchers have insisted on the importance of
54 adsorption and/or co-precipitation in the process of aqueous contaminant removal by Fe⁰
55 (Burriss et al., 1995; Allen-King et al., 1997; Lackovic et al., 2000; Lavine et al., 2001;
56 Furukawa et al., 2002; Ritter et al., 2002; Wilkin and McNeil, 2003; Su and Puls, 2004;
57 Mielczarski et al., 2005). However, their argumentation was limited either (i) to inorganic
58 contaminants (e.g. Lackovic et al., 2000; Wilkin and McNeil, 2003), (ii) to selected organic
59 species (e.g. Mielczarski et al., 2005) or (iii) to investigations on the impact of iron corrosion
60 products as contaminant scavengers (Furukawa et al., 2002, Jia et al. 2007) or reducing agents
61 (Refait et al., 1998; Ritter et al., 2002; O'Loughlin et al., 2003; O'Loughlin and Burriss, 2004;
62 Chaves, 2005 ; Liang and Butler, 2011). For example, Furukawa et al. (2002) stated that
63 under oxic conditions, ferrihydrite may be one of the most abundant iron corrosion products
64 and may play an important role in adsorbing contaminants. In such situations, the use of Fe⁰
65 reactive walls "may be extended to applications that require contaminant adsorption rather
66 than, or in addition to, redox-promoted contaminant degradation". On the other hand, the
67 findings of Lackovic et al. (2000) that arsenic is not removed by a reductive transformation
68 process war clearly presented as an exception. It is important to note that results from the very
69 first peer-reviewed articles on the Fe⁰/H₂O systems where uncertain about the real

70 mechanisms of contaminant removal (Table 1). However, the hypothesis of contaminant
71 reduction was favored without experimental proofs (e.g. mass balance) (e.g. Lee et al., 2004).
72 As stated by O'Hannesin and Gillham (1998), it was a "broad consensus".

73 The kit of tools to investigate contaminant reduction includes a large number of highly
74 sophisticated instruments for determining contaminant concentration and speciation,
75 identifying contaminant reaction products and iron corrosion products as well (McGuire et al.,
76 2003). Further used tools aimed at properly model experimental data and thus design field Fe⁰
77 treatment units (e.g. field reactive walls, household filters) (Schüth et al., 2003; VanStone et
78 al., 2005; Li et al., 2006; Kouznetsova et al., 2007; Klammler and Hatfield, 2008; Li and
79 Benson, 2010; Jeon et al., 2011). Additionally, researchers were organized in networks (e.g.
80 PRBT - the US Permeable Reactive Barriers Action Team; RUBIN - the German Permeable
81 Reactive Barrier Network; PRB-Net - the Permeable Reactive Barrier Network in the United
82 Kingdom) having the goal to accelerate the development of the promising Fe⁰ technology.
83 Thus, it would seem that the role of reductive transformation in the process of contaminant
84 removal by Fe⁰ fulfils all of the criteria for a true paradigm.

85 It should be acknowledged that the reductive transformation concept has been a fruitful
86 paradigm, fueling substantial progress for the achieved acceptance of the Fe⁰ technology
87 (Bigg and Judd, 2000; Scherer et al., 2000; Henderson and Demond, 2007; Laine and Cheng,
88 2007; Cundy et al., 2008; Thiruvengkatachari et al., 2008; Groza et al., 2009; Muegge and
89 Hadley, 2009; Phillips et al., 2010). Nevertheless, a growing body of evidence indicates that
90 factors other than reductive transformations contribute importantly to the process of
91 contaminant removal in Fe⁰/H₂O systems. These factors included adsorption, co-precipitation
92 and adsorptive size exclusion.

93 **2 Limits of the reductive transformation concept**

94 Concordant reports on enhanced Fe⁰ reactivity towards aqueous contaminant removal with
95 decreasing particle size have been reported. As a consequence nano-scale Fe⁰ (nano-Fe⁰) has
96 been suggested and is currently injected in the subsurface for groundwater remediation (Wang
97 and Zhang, 1997; Comba et al., 2011; Shi et al., 2011). Another common tool to enhance Fe⁰
98 reactivity is the use of bimetallic materials (Fe/Cu, Fe/Ni, Fe/Pd) (Muftikian et al., 1995).
99 However, neither the use of nano-Fe⁰ (Noubactep and Caré, 2010a) nor that of bimetallic
100 systems (Noubactep, 2009a) is consistent with the fact that contaminants should be reduced
101 by Fe⁰. While the plating metal (e.g. Cu⁰, Ni⁰, Pd⁰) are concurrent reagents for Fe⁰ oxidation,
102 nano-Fe⁰ will be readily oxidized by water which is in stoichiometric excess relative to

103 dissolved contaminants. These both facts (“anomalies”) are the first arguments against the
104 view that contaminants are quantitatively removed by reductive transformations.

105 Several other experimental results seem to have stretched the reductive transformation
106 paradigm to the point where it may no longer be intellectually satisfying. Among these results
107 (Noubactep, 2007; Noubactep, 2010a, Scott et al. 2011 and ref. therein): (i) the quantitative
108 removal of species like Zn^{II} which is not reducible by Fe^0 or the quantitative removal of Mo^{VI}
109 which is not readily adsorbed on iron oxides (at $pH > 6$), (ii) the quantitative removal of
110 organic species in Fe^0 beds which were proven non reducible by Fe^0 in batch systems (Lai et
111 al., 2006), (iii) the existence of the lag time in the process of contaminant removal in batch
112 systems (Schreier and Reinhard, 1994; Hao et al., 2005). Where the reductive transformation
113 paradigm is not useful, researchers have favored selective adsorption or microbial processes
114 to explain observed results (Lai et al., 2006). However, this approach can be regarded as a
115 falsification of the reductive transformation paradigm since it assumed that adsorption is only
116 important when reduction is not favorable. Moreover, contaminant co-precipitation with
117 precipitating and transforming iron oxides is considered only for specific cases as discussed
118 above. This is the juncture (proliferation of anomalies) at which Kuhn observes that
119 paradigms tend to shift (Heaney, 2003).

120 The expression "paradigm shift" is believed to be misused or overused in science. For this
121 reason this communication proposes that the reductive transformation paradigm is giving way
122 to a successor that seems to provide an operationally superior and an intellectually more
123 attractive rationalization of the process of aqueous contaminant removal by Fe^0 .

124 It must be acknowledged that the principle that contaminants are quantitatively removed in
125 Fe^0/H_2O systems has never been in question. The sole discussion is about the occurrence of
126 reduction (if applicable) and its extent (Lee et al., 2004). The next section will briefly present
127 a different view on the process of contaminant removal which is the essence of the alternative
128 paradigm. The new concept suggests in analogy with the historical work of Yao et al. (1971)
129 that contaminants are collected in Fe^0 beds (deep bed filters) by in situ generated Fe^{II}/Fe^{II-}
130 species regardless if they are chemically transformed or not.

131 **3 Adsorption/co-precipitation concept**

132 The concept that contaminants are fundamentally adsorbed and/or co-precipitated onto/with
133 iron corrosion products in Fe^0/H_2O systems is extensively presented in several recent articles
134 (e.g. Noubactep, 2010a; 2010b; 2011). The concept arose from a fortuitous observation during
135 experiments on the process of uranium removal in “ $Fe^0/MnO_2/H_2O$ ” systems [“ Fe^0 ”, “ MnO_2 ”
136 and “ $Fe^0 + MnO_2$ ”] (Noubactep et al., 2003) and is supported by results from all other

137 branches of science involving aqueous iron corrosion (Noubactep, 2009b; Noubactep and
138 Schöner, 2009; Noubactep and Schöner, 2010).

139 In the mentioned experiments, MnO₂ and waterworks sludge (aged iron oxides – Fe₂O₃) were
140 used as relevant adsorbents and their impact on the process of U^{VI} removal by Fe⁰ was
141 characterized. Results showed that none of the adsorbents could significantly accelerate U^{VI}
142 removal. Moreover, MnO₂ essentially retarded U^{VI} removal and the lag time was proportional
143 to the available amount of MnO₂. These results indicated that U^{VI} is mostly removed by in-
144 situ generated iron corrosion products. Aged Fe₂O₃ could not significantly impact U^{VI}
145 removal. MnO₂ essentially retarded the removal process. This delay is due to the fact that iron
146 hydroxides are not precipitated in the vicinity of Fe⁰ but rather at the surface of MnO₂. The
147 process of reductive dissolution of MnO₂ by Fe^{II} is a well-documented geochemical process
148 (Stone, 1987; Stone and Ulrich, 1989; Postma and Appelo, 2000; Kang et al., 2006).

149 A close consideration of the impact of MnO₂ on the process of U^{VI} removal by Fe⁰ suggested
150 that U^{VI} removal is a characteristic of corroding iron. In other words, U^{VI} removal is not
151 necessarily a reductive process or a result of any specific interactions between U^{VI} and Fe⁰.
152 Specific interactions between contaminants and Fe⁰ (and iron oxides) will certainly favour the
153 removal process but are not the determinant factors (Scott et al., 2011). Accordingly, a
154 Fe⁰/H₂O system can be regarded as a domain of precipitating iron hydroxide (Noubactep,
155 2009c). In such a system, any inflowing contaminant will be adsorbed and co-precipitated.
156 Additionally, Fe^{II} and H/H₂ from continuously corroding Fe⁰ are reducing agents for reducible
157 contaminants in the system but the extent of contaminant reduction is difficult to discuss
158 because generated iron oxides must be digested for contaminant speciation and mass balance
159 calculations. On the other hand, contaminants enmeshed in the matrix of iron corrosion are
160 stable for long time under environmental conditions whether they are chemically transformed
161 or not (Noubactep et al. 2006).

162 The presentation above has explained why all classes from aqueous contaminants may be
163 quantitatively removed by Fe⁰. It is clear from this presentation that parent contaminants and
164 their reaction products are all removed in Fe⁰/H₂O systems. This is consistent with view that
165 in a Fe⁰ bed in situ generated Fe hydroxides and oxides act as contaminant “collectors” (Yao
166 et al., 1971). Accordingly, one of the three major opened problems (how can harmful reaction
167 products be removed?) from the reductive transformation concept is solved. The remaining
168 two problems are: (i) How can reactivity loss be prevented? and (ii) How can permeability
169 loss be properly considered? Answering these questions is over the scope of this
170 communication. However, it should be pointed out that recent theoretical works have shown

171 that to sustain system permeability, Fe^0 should be admixed to inert materials in a volumetric
172 ratio lesser than 52 %. In other words an efficient Fe^0 bed could be regarded as a Fe^0 amended
173 sand filter. A proposed tool to sustain reactivity is to use Fe^0/MnO_2 mixtures (Noubactep et
174 al., 2010).

175 The concept presented in this section clearly belittles the importance of reduction in the
176 process of aqueous contaminant removal in $\text{Fe}^0/\text{H}_2\text{O}$ systems. There is increasing evidence
177 that this concept is not yet understood by authors which have referenced related papers. The
178 next section will address this issue.

179 **4 Argumentation against the new concept**

180 The concept regarding adsorption and co-precipitation as the fundamental mechanisms of
181 contaminant removal in $\text{Fe}^0/\text{H}_2\text{O}$ systems has been experimentally validated using methylene
182 blue as model contaminant (Noubactep, 2009d). The concept has recently been verified using
183 clofibric acid (Ghauch et al., 2010a) and diclofenac (Ghauch et al., 2010b). Moreover, the
184 similitude between contaminant removal with elemental metals and electrocoagulation has
185 been excellently presented by Bojic et al. (2004; 2007; 2009). Nevertheless, there are
186 currently five types of arguments in the literature belittling the significance of this concept: (i)
187 the concept is wrongly referenced (Luna-Velasco et al., 2010; Yuan et al., 2010) (**argument**
188 **1**), (iia) the concept is hardly acceptable because the reductive transformation concept is
189 widely accepted in the scientific community, (iib) self-citation is always used to support the
190 validity of the new the concept (Kang and Choi, 2009) (**argument 2**), (iii) Good results on
191 removal of inorganic species by Fe^0 are unacceptably generalized (Ebert et al., 2007;
192 Tratnyek and Salter, 2010) (**argument 3**), (iv) data are needed to support the repeated claims
193 which negate more than one decade intensive research (Ebert et al., 2007; Tratnyek and
194 Salter, 2010) (**argument 4**), and (v) authors of the correct references deliberately further
195 referenced the concept or not (**argument 5**). For example, Flury and his colleagues (Flury et
196 al., 2009a; 2009b) referenced Noubactep (2006) in a paper for Applied Geochemistry
197 (available online 24 December 2008) and not in the paper for Environmental Science &
198 Technology (accepted May 14, 2009). In the meantime, three other more elaborated papers on
199 the new concept were available. Second example: Lo and co-workers have correctly
200 referenced the concept in 2008 (Rao et al., 2009 - accepted 11 December 2008) and not in
201 several subsequent works (e.g. Liu et al., 2009, Mak et al., 2009; 2011). Short comments on
202 individual arguments will be given bellow.

203 **Argument 1:** The concept was introduced in 2007 in an open access journal (Noubactep,
204 2007). There is no reason why so many researchers could ignore or wrongly reference it.

205 Referencing articles using or presenting the new concept, co-precipitation is enumerated as a
206 “simple” reaction mechanism beside adsorption and reduction (Luna-Velasco, et al. 2010;
207 Yuan et al., 2010). The fact, that researchers are ignoring the state-of-the-art knowledge on
208 the mechanism of contaminant removal in $\text{Fe}^0/\text{H}_2\text{O}$ systems should be a concern for the whole
209 community.

210 **Argument 2:** The consistency of the concept of reductive transformation has been extensively
211 discussed while introducing the concept of adsorption/co-precipitation. Researchers should
212 have discussed the validity of the new concept instead of simply doubt on its validity.
213 Fortunately, Dr. Ghauch who was initially sceptic about the adsorption/co-precipitation
214 concept (Ghauch, 2008b) has experimentally verified its efficiency to explain processes which
215 are still mistakenly attributed to plated Fe^0 (Ghauch et al., 2010b).

216 **Argument 3:** Not all inorganic substances are readily adsorbed onto iron oxides (iron
217 corrosion products) (Blowes et al., 2000). For example, Mo^{VI} is very poorly adsorbed on iron
218 oxides at $\text{pH} > 6.0$ (Scott et al., 2011 and references therein) but was reported to be
219 successfully removed by Fe^0 (Morrison et al., 2002; 2006). On the other hand, many organic
220 compounds are readily adsorbed onto iron oxides (Tipping and Higgins, 1982; Tipping, 1986;
221 Gu et al., 1994, Satoh et al., 2006; Hanna and Boily, 2010; Eusterhues et al., 2011). Besides
222 these hard facts from the geochemical literature, it has been clearly demonstrated that
223 contaminant removal is not primarily a property of contaminants but rather a characteristic of
224 aqueous iron corrosion. In other words, contaminants are not removed by Fe^0 or Fe oxides
225 separately, but during the whole dynamic process of aqueous iron corrosion. In Fe^0 beds,
226 adsorptive size exclusion in a deep bed filtration mode sustains the removal efficiency. The
227 argument of self-citation is not acceptable because nobody else has systematically reported on
228 the inconsistency of the reductive transformation concept. Moreover, authors like Burris et al.
229 (1995), Lavine et al. (2001), Mantha et al. (2001), and Odziemkowski (2009), who have
230 seriously questioned some aspects of the reductive transformation concept, have been
231 constantly referenced.

232 **Argument 4** is mostly used by reviewers and referees who have rejected several manuscripts
233 and proposals. Rejected manuscripts were subsequently accepted by other reviewers
234 sometimes from the same journal in a new submission. It is important in this regard to notice
235 that many reviewers have argued that the reviews presenting the concept adsorption/co-
236 precipitation could have never been published in ISI referenced journals (Noubactep, 2006;
237 2007) or in journals with higher impact factor (Noubactep, 2008) because of its poor scientific
238 quality. While manuscripts could be revised and re-submitted, proposals have been

239 systematically rejected. This is a well-known situation whenever a new view is introduced
240 (Alm, 1992; Heaney, 2003).

241 **Argument 5** suggests that the ground-breaking nature of the concept was not clear to the
242 authors who may have been prompted by peer-reviewers to reference related works.

243 The comments above showed that no single valid argument against the adsorption/co-
244 precipitation concept has yet been presented. Moreover, theoretical studies related to this
245 concept are a powerful guide for appropriate experimental designs (Noubactep and Caré,
246 2010a; 2010b; 2010c; Noubactep et al., 2009; Noubactep et al., 2010; Noubactep and Caré,
247 2011). On the other hand, regarding Fe⁰ beds as "Fe⁰ amended sand filters" suggests that
248 population balance models that account for pore and particle size distributions along with
249 pore space topology (e.g. Bedrikovetsky, 2008) describe processes in dynamic Fe⁰/H₂O
250 systems with better accuracy than currently used models (Jeen et al. 2011).

251 **5 Concluding remarks**

252 The use of Fe⁰ for water treatment was based on the thermodynamic valid argument that Fe⁰
253 is a relative strong reducing agent ($E^0 = -0.44$ V/ESH). However, this assumption has
254 overseen at least two important aspects of aqueous iron corrosion and their thermodynamics:
255 (i) solubility of iron hydroxides, and (ii) adhesion of oxide scale on metal (Noubactep, 2010a;
256 2010b). In fact, whether contaminant reduction by Fe⁰ (direct reduction) occurs and
257 contributes significantly to the process of contaminant removal remains unclear. However, it
258 is certain that several groups of contaminants are quantitatively removed in Fe⁰/H₂O systems
259 and that these contaminants are adsorbed and co-precipitated (Noubactep, 2009d; Ghauch et
260 al., 2010a; 2010b). Adsorbed and co-precipitated contaminants could be further reduced by
261 electrons from Fe⁰ (direct reduction) but more likely by electrons from Fe^{II} or H/H₂ (indirect
262 reduction). Additionally, some contaminants could be oxidized in the systems by in-situ
263 generated Fenton-like reagents (Ghauch et al., 2010b). It is the aim of this communication to
264 propose the substitution of the reductive transformation concept by the one of adsorption/co-
265 precipitation (and adsorptive size-exclusion).

266 It has been argued that "no paradigm passes painlessly" (Heaney, 2003). The scientific
267 objectivity should dictate the fate of any scientific concept regardless from its age or what has
268 been invested in it. To the author's opinion, the proposed paradigm shift does not represent a
269 danger for any industry but rather a chance for more systematic system designs. For example
270 the elimination of the constrains that contaminants should be reduced implies that surrogate
271 parameters (e.g. dissolved organic carbon - DOC) can be used to monitor effluents for
272 organics from treatment systems until breakthrough occurs. Afterwards more precise analytic

273 tools are needed to identify escaped organic species. On the other hand, the proposed new
274 paradigm has enabled a better bed design and clarified the controversial issue of using inert
275 admixture in Fe⁰ beds (Noubactep et al., 2010). Furthermore, the new paradigm is about to re-
276 vive Fe⁰ household filters, e.g. the 3-Kolshi filters (Khan et al., 2000; Hussam and Munir,
277 2007; Hussam, 2009). The 3-Kolshi filters have been abandoned because of poor design as
278 recently demonstrated (Noubactep et al., 2010). The 3-Kolshi filters were replaced by very
279 sustainable filters (SONO filters) in which iron shavings/fillings were substituted by a porous
280 Fe⁰-based composite (Hussam and Munir, 2007; Hussam, 2009).

281 The adsorption/co-precipitation concept has demonstrated that reduction is less important for
282 the process of contaminant removal than had been assumed. Because contaminants are
283 progressively enmeshed in the matrix of iron corrosion products, they are even more stable
284 than if they were simply reduced or degraded. Accordingly, the proposed paradigm even
285 sustains the acceptance of the Fe⁰ technology. Actually, nobody is in appreciable jeopardy
286 from the paradigm shift in course. Researchers are given more possibilities for rationale and
287 systematic investigations of contaminant removal in Fe⁰/H₂O systems as they could partly
288 paid less attention to contaminant speciation. It is hoped that this opportunity will be used for
289 a rapid development of the Fe⁰ technology and its extension to other applications as recently
290 suggested by Antia (2010).

291 In conclusion, enhanced collaboration between experimental and modelling scientists is
292 needed in order to expedite resolution of the key gaps in the understanding of the operation of
293 processes governing the functionality of Fe⁰ filtration systems. This closed collaboration is
294 essential to frame new Fe⁰ bed models.

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596

596 **Table 1:** Overview on important results of the four first published peer-reviewed articles on
 597 the Fe⁰/H₂O system (1994) and the number of their citations in Scopus (2011/03/27). It can be
 598 seen that none of these seminal works has demonstrated quantitative contaminant reduction.
 599 Moreover, the least cited work is the one which has created conditions for favorable
 600 contaminant reduction (acidification by FeS₂). X stands for contaminant; RCl is a chlorinated
 601 hydrocarbon.

602

Reference	Systems	X	Findings	Citations
Matheson and Tratnyek	Fe ⁰ /H ₂ O	CH _x Cl _y	Degradation mostly by Fe ⁰	616
Gillham and O'Hannesin	Fe ⁰ /H ₂ O	RCl	Enhanced degradation	597
Schreier and Reinhard	Fe ⁰ /H ₂ O	C ₂ Cl ₄	Partial degradation	65
Lipczynska-Kochany et al.	Fe ⁰ /FeS ₂ /H ₂ O	CCl ₄	FeS ₂ accelerates degradation	49

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604