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Advances in surface passivation of nanoscale zerovalent iron (NZVI): A critical review

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24 **ABSTRACT**

25 Nanoscale zerovalent iron (NZVI) is one of the most extensively studied nanomaterials in
26 the fields of wastewater treatment and remediation of soil and groundwater. However, rapid
27 oxidative transformations of NZVI can result in reduced NZVI reactivity. Indeed, the surface
28 passivation of NZVI is considered one of the most challenging aspects in successfully
29 applying NZVI to contaminant degradation. The oxidation of NZVI can lead to the formation
30 of Fe^{II}-bearing phases (e.g., Fe^{II}O, Fe^{II}(OH)₂, Fe^{II}Fe^{III}₂O₄) on the NZVI surface or complete
31 oxidation to ferric (oxyhydr)oxides (e.g., Fe^{III}OOH). This corrosion phenomenon is dependent
32 upon various factors including the composition of NZVI itself, the type and concentration of
33 aqueous species, reaction time and oxic/anoxic environments. As such, the co-existence of
34 different Fe oxidation states on NZVI surfaces may also, in some instances, provide a unique
35 reactive microenvironment to promote the adsorption of contaminants and their subsequent
36 transformation via redox reactions. Thus, an understanding of passivation chemistry, and its
37 related mechanisms, is essential not only for effective NZVI application but also for
38 accurately assessing the positive and negative effects of NZVI surface passivation. The aim of
39 this review is to discuss the nature of the passivation processes that occur and the passivation
40 byproducts that form in various environments. In particular, the review presents: i) the
41 strengths and limitations of state-of-the-art techniques (e.g., electron microscopies and X-ray
42 based spectroscopies) to identify passivation byproducts; ii) the passivation mechanisms
43 proposed to occur in anoxic and oxic environments; and iii) the effects arising from synthesis
44 procedures and the presence of inorganics/organics on the nature of the passivation
45 byproducts that form. In addition, several depassivation strategies that may assist in
46 increasing and/or maintaining the reactivity of NZVI are considered, thereby enhancing the
47 effectiveness of NZVI in contaminant degradation.

48

49 1. INTRODUCTION

50 In recent decades, zerovalent iron (ZVI, Fe(0)) has been extensively studied for its
51 capacity to transform contaminants in soils, groundwater and industrial wastewaters because
52 of: (i) its ability to reductively transform a wide variety of compounds, such as halogenated
53 organics, into less toxic and/or more biodegradable forms; (ii) the abundance of iron (the
54 fourth most abundant element in the earth's crust); (iii) the relative environmental friendliness
55 of an iron-based technology compared to other zerovalent metals (such as Mn(0) and Cu(0))
56 and (iv) the low cost of Fe⁰ mass production.¹⁻⁷ In particular, nanoscale zerovalent iron (NZVI)
57 has attracted attention due to the potential advantages arising from high particle reactivity
58 (resulting from the small size and high surface area of NZVI) when compared to ZVI.^{3-6,8-21}
59 Moreover, NZVI has been confirmed to reductively remove various organic (e.g., chlorinated
60 aliphatic^{3,6,8-10} and aromatic compounds^{10,11,13,14}), inorganic (e.g., nitrate,¹² Cr(VI),¹⁷ As(III)¹⁸⁻
61 ²² and Cd(II)²³) and radioactive (e.g., U(VI)²⁴⁻²⁶ and Tc(VII)²⁷) contaminants under anoxic
62 conditions. It has also been demonstrated that NZVI can induce the oxidative degradation of
63 organic contaminants (e.g., pharmaceuticals^{28,29} and herbicides^{30,31}). This may occur as a
64 result of the reduction of dissolved oxygen (O₂) and the associated production of hydrogen
65 peroxide (H₂O₂) that subsequently reacts with Fe(II) (that is also produced during oxidation)
66 leading to initiation of the Fenton reaction (Fe(II) + H₂O₂ → Fe(III) + HO* + OH⁻) and the
67 generation of strongly oxidizing hydroxyl radicals (HO*, 2.80 V).

68 Typical NZVI particles have a core-shell (Fe(0)-Fe (oxyhydr)oxide) structure with the
69 spherical nanosized primary particles forming chain-like aggregates with sizes ranging up to a
70 few micrometers.³ Moreover, the aggregates exhibit the magnetic properties of the primary
71 particles with the magnetism of the primary particles influencing the size and structure of
72 these assemblages.³² The co-existence of the Fe(0) core and oxidized Fe surface layer
73 provides a unique reactive surface for the initial adsorption of contaminants and their

74 subsequent transformation on the particle surface via reductive or oxidative
75 pathways.^{3,5,14,16,29,30} In accordance with contaminant adsorption, oxidation or reduction, Fe
76 may undergo oxidation (from Fe(0) to Fe(II) and Fe(II) to Fe(III)), precipitation (as Fe(II)
77 and/or Fe(III) solids) and, possibly, co-precipitation with ionic species.^{8,33–35} Concomitantly,
78 it may also be necessary to consider reactions with other solution phase entities such as O₂,
79 (which, as noted above, may be reduced to H₂O₂, possibly due to adsorption to NZVI or its
80 (oxyhydr)oxide-coated surface),^{28,29} sulfate (which may possibly be reduced to sulfide,
81 resulting in the formation of FeS solid phases on the NZVI surface)³⁵ and carbonate (which
82 may also promote the precipitation of ferrous carbonate minerals).³⁶

83 Many researchers have demonstrated that NZVI undergoes surface oxidation (or surface
84 passivation) when used for the removal of contaminants in variably oxic environments.^{3,6,8,29}
85 In addition, a field study has shown that 78–97% of Fe(0) injected was oxidized in a sediment
86 sample after 165 d at a remedial site contaminated with a dense non-aqueous phase liquid
87 (DNAPL).³⁷ Investigations have revealed that, depending on the environmental conditions
88 and types of contaminants present, NZVI surface layers (and eventually, the bulk of the solid)
89 transform to different Fe mineral phases, such as vivianite (Fe^{II}₃(PO₄)₂·8H₂O), Fe(OH)₂,
90 green rust (Fe(II)-Fe(III) layered double hydroxides with various interlayer anions (e.g. Cl⁻,
91 SO₄²⁻ and CO₃²⁻)), ferrihydrite, magnetite (Fe^{II,III}₂O₄), lepidocrocite (γ-Fe^{III}OOH), goethite (α-
92 Fe^{III}OOH), mackinawite (Fe^{II}S), and siderite (Fe^{II}CO₃), as presented in Table 1. Moreover,
93 NZVI can be completely transformed to lepidocrocite in oxygenated water³⁸ and partially
94 transformed to Fe(OH)₂ in O₂-free water in the absence of contaminants.³⁹ The passivation
95 kinetics and the nature of the products generated have a significant influence on the long-term
96 viability of the technology given that Fe(II)-containing minerals such as magnetite,^{40–43}
97 vivianite,^{44–47} and green rust^{48–50} and surface-bound Fe(II)^{51,52} can further remove organic and
98 inorganic contaminants. In addition, Fe(III)-containing minerals (e.g., maghemite (γ-Fe₂O₃),⁵³

99 goethite⁵⁴ and hematite⁵⁵) can effectively remove contaminants via sorptive effects. For
100 example, it has been reported that, in anoxic conditions, passivated NZVI demonstrated
101 similar or slightly higher sorptive ability for perfluoroalkyl acids⁵⁶ and As(V)⁵⁷ when
102 compared to fresh NZVI. These results are most likely due to the presence of a greater
103 number of adsorption sites on the Fe (oxyhydr)oxides passivating the NZVI surface compared
104 to the number of sites on pristine NZVI. These findings imply that passivation byproducts of
105 NZVI can potentially act as reactants for the further removal of contaminants, even after the
106 depletion of the initial NZVI.

107 Although the positive effects of passivation are evident, there are several adverse effects
108 to the formation of passivation byproducts on NZVI that should be considered (in addition to
109 reduced activity). The production of reactive oxygen species (ROS) in NZVI suspensions, as
110 previously mentioned, was considered to account for the high toxicity of fresh NZVI to rodent
111 neuron and microglia cells when compared to the limited effect of aged NZVI and magnetite
112 nanoparticles⁵⁸ with the severity of toxicity related to the iron oxidation state with Fe(0) >
113 Fe(II) > Fe(III).⁵⁹ The toxicity of passivation byproducts from NZVI may be lower than that
114 of NZVI however the results of the above studies suggest that the passivation byproducts (i.e.,
115 Fe(II) and Fe(III) species) can also induce secondary toxic effects. In addition, it has been
116 suggested that the presence of nanoparticles may enhance the transport of contaminants
117 associated with these nanoparticles,⁶⁰ though certain reports suggest that the mobility of NZVI
118 particles is likely to be retarded as a result of the association of these particles with subsurface
119 sediments.^{61,62} Therefore, an understanding of passivation kinetics, transformation byproducts
120 and related mechanisms is required when considering the reactivity, longevity and stability of
121 NZVI.

122 Although a number of reviews regarding NZVI have been published, most reviews have
123 focused on NZVI synthesis and characterization, application to the removal of contaminants

124 or implementation and results of field studies.^{15,63-74} In comparison, in this review, we
125 introduce: (i) common characterization techniques for determining the nature of passivation
126 byproducts; (ii) insights into the passivation mechanism(s) underlying observed structural
127 transformations of NZVI in oxic and anoxic environments and (iii) the effect of synthesis
128 methods and solution conditions such as the presence of various organic and inorganic species
129 on the passivation process. In addition, we describe various depassivation strategies that could
130 potentially be used to either prevent or retard passivation processes and thereby extend the
131 lifetime over which NZVI is an effective agent for the degradation of contaminants.

132

133 **2. CHARACTERIZATION OF NZVI PASSIVATION BYPRODUCTS**

134 To identify the NZVI passivation mechanism operating under specific conditions, the
135 investigation and monitoring of the formation of passivation byproducts throughout and after
136 the passivation process are required. In this section, common techniques used for identifying
137 passivation byproducts are reviewed and the benefits and limitations of each technique are
138 discussed. The primary methods of interest include electron microscopy, X-ray diffraction
139 (XRD), X-ray photoelectron spectroscopy (XPS), Raman and Mössbauer spectroscopies and
140 X-ray absorption spectroscopy (XAS).

141

142 **2.1. Electron Microscopy**

143 Transmission and scanning electron microscopy (TEM and SEM) have been the most
144 widely used techniques to determine the morphological characteristics of NZVI passivation
145 byproducts. TEM can provide visual information at the nanoscale level of properties such as
146 the core size of fresh NZVI, the thickness of the passivating layer after partial passivation, and
147 morphological changes after complete structural transformation. Additionally,
148 crystallographic information including crystallinity and lattice spacing can be obtained using

149 selected area electron diffraction.^{36,39} For fresh NZVI, a spherically-shaped core-shell
150 structure is commonly observed using TEM. The size of the core is typically within a range of
151 tens of nanometers with the core covered by a thin Fe (oxyhydr)oxide layer of several
152 nanometers thickness as shown in Figure S1.^{3,8,19,38,75} After surface passivation,
153 morphological changes in the NZVI structure can be detected using TEM. Typical changes
154 include loss of the Fe(0) core and the appearance of hollow (oxyhydr)oxide shells with this
155 transformation reported to occur within 24 h under oxic conditions.³⁸ Further aging to 72 h
156 can result in the formation of flake- or acicular-shaped minerals (such as lepidocrocite).³⁸

157 Another effective analytical technique typically associated with TEM is X-ray energy
158 dispersive spectroscopy (XEDS). The results of XEDS can provide the elemental composition
159 of passivation byproducts and can support identification of the Fe mineral phases present,
160 especially when certain elements such as P and S are co-localised in minerals such as
161 (respectively) vivianite ($\text{Fe}_3(\text{PO}_4)_2$) and mackinawite (FeS).^{33,34,35} In recent times, scanning
162 TEM (STEM)-XEDS has been used to identify the passivation mechanism that occurs in
163 single nanoparticles by the acquisition of nanoscale images and elemental maps.^{36,38,76} For
164 instance, the growth of amorphous assemblages within the NZVI core with subsequent
165 transformation to plate-like crystalline forms has been observed using STEM (Figures 1(a-c)).
166 These results can then be matched to XEDS maps to reveal a decrease and increase,
167 respectively, in the Fe and O contents within the NZVI core.³⁶

168

169 **2.2. X-ray Diffraction (XRD)**

170 X-ray diffraction is one of the most popular analytical techniques for characterizing the
171 particular minerals that form upon NZVI passivation.¹⁵ It is particularly useful for identifying
172 crystalline phases that give sharp and characteristic diffraction peak patterns. Most studies in
173 which the mineralogy of passivated NZVI has been examined by XRD have typically been

174 limited to analyses ‘before’ and ‘after’ reaction of the sample with very limited insight gained
175 into the kinetics of mineral transformations.^{22,77–79} A large number of iron crystalline phases
176 have been identified by XRD in passivation byproduct studies however lepidocrocite and
177 magnetite/maghemite are overwhelmingly the dominant phases detected.¹⁵ The latter two
178 minerals cannot be identified separately by XRD as both have indistinguishable diffraction
179 patterns despite their different oxidation states. Other less common NZVI passivation
180 byproducts detected by XRD include ferrihydrite,⁷⁷ goethite,⁸⁰ vivianite,^{33,34} amakinite
181 ($\text{Fe}^{\text{II}}(\text{OH})_2$),⁸¹ hematite,¹⁸ chukanovite ($\text{Fe}^{\text{II}}_2(\text{OH})_2\text{CO}_3$)⁸² and carbonate green rust.⁸³

182 Perhaps the most significant limitation of using XRD to identify passivation byproducts
183 is that some minerals, including NZVI itself, quite often present as X-ray amorphous and/or
184 only display broad diffraction peaks.¹⁵ In addition, the mineral detection limits for XRD are in
185 the order of 2 to 3 wt. %.¹⁵ Thus, quantitative analysis of the relative proportions of minerals
186 present could be difficult or impossible with this analytical approach. This could possibly
187 explain why the very common nanocrystalline, X-ray amorphous mineral ferrihydrite has
188 rarely been identified as a major passivation byproduct in NZVI studies in which XRD was
189 used as the primary characterization technique.

190

191 2.3. X-ray Photoelectron Spectroscopy (XPS)

192 X-ray photoelectron spectroscopy is a surface sensitive technique that can be used to
193 characterize several nanometers of the NZVI outer layer. Although it is difficult to
194 conclusively determine the nature of the NZVI passivation byproducts using XPS due to the
195 limited information that can be obtained on the mineral phases, this technique can provide
196 important information on the nature of the elements present at the NZVI surface including
197 their oxidation states. The kinetic energy and number of electrons emitted from irradiation of
198 the surface by X-rays of known energy are measured during XPS analysis. For the

199 determination of the oxidation state of elements present within the surface layer, the narrow
200 peaks for the Fe(2p_{3/2}) and O(1s) binding energies are particularly useful.^{8,40,84} A
201 comprehensive understanding of the oxidation states of the Fe and O species on the NZVI
202 surface can provide critical information on passivation byproducts.^{38,84–86} For example, the
203 presence of an Fe(0) peak at ~706 eV indicates that the core Fe(0) is preserved because XPS
204 is sensitive to the outermost layer of the particles.⁶ In addition, it has been reported that after
205 72 h reaction with oxygenated water, NZVI passivation byproducts displayed peaks of Fe at
206 ~711 eV and O at ~530 eV and 531 eV, indicating the presence of Fe₂O₃, Fe₃O₄ and/or
207 FeOOH.³⁸

208

209 **2.4. Raman and Mössbauer Spectroscopies**

210 Raman spectroscopy can be carried out *in situ* to monitor the formation of NZVI
211 passivation byproducts, particularly when the minerals to be identified are poorly crystalline.
212 However, the transformation of Fe (oxyhydr)oxides as a result of laser-induced thermal
213 heating may complicate interpretation of results.⁷⁷ For example, hematite is often detected by
214 Raman spectroscopy but absent in corresponding XRD data.^{77,78} In the early stages of NZVI
215 aqueous oxic corrosion, wustite (Fe^{II}O) can be detected by Raman spectroscopy (~595 cm⁻¹)⁷⁸.
216 It is an unstable intermediate phase generally formed in small amounts below the
217 detection limit of XRD. At longer aging times (e.g. 30 d in static deionized water or 24 h in
218 deionized water mixed at 300 rpm), Raman analyses have revealed the simultaneous co-
219 existence of maghemite (665 and 730 cm⁻¹), magnetite (670 cm⁻¹) and lepidocrocite (650 cm⁻¹).^{77,78}
220 On prolongation of NZVI aging time to 60–90 d in static water or 48–72 h in stirred
221 water, only lepidocrocite (250, 380, 526 and 650 cm⁻¹) was identified (in close agreement
222 with XRD results).³⁸ Raman analysis has been used to show that aging under anoxic
223 conditions favors the formation of wustite, goethite and akaganeite (β-Fe^{III}OOH).⁷⁸

224 ⁵⁷Fe Mössbauer spectroscopy can be used for detecting Fe atoms in different oxidation
225 states and is a useful technique to identify the nature of any amorphous mineral phases present.
226 Mössbauer spectroscopy can provide relevant information on the valency and spin states of Fe
227 species as well as their magnetic properties via analysis of the hyperfine parameters. As such,
228 magnetite and maghemite can be distinguished using this technique. Moreover, it can be used
229 to determine the percentages of elemental Fe(0) and other secondary minerals that are
230 present.⁶³ The typical ⁵⁷Fe Mössbauer spectrum of ZVI exhibits a single magnetic component
231 corresponding to Fe(0) with hyperfine parameters corresponding to a cubic phase of metallic
232 Fe. However a simple spectrum of this nature has rarely been observed for NZVI, even when
233 the NZVI was pristine and freshly- prepared.^{19,63,87} Typically, a complex hyperfine structure is
234 observed with at least five components: a magnetic sextet with narrow lines corresponding to
235 that of Fe(0), two quadruple components corresponding to Fe(III) and Fe(II) species, and two
236 magnetic components. Mössbauer specialists suggest that these results are indicative of the
237 presence of disordered ferric (oxyhydr)oxides (e.g., Fe(OH)₃) and/or superparamagnetic ferric
238 oxides (e.g., Fe₃O₄) on the passivated surface of Fe(0). When NZVI reacts with contaminants
239 in water, a quadruple doublet and a magnetic sextet with broadened lines are commonly
240 observed and have generally been attributed to the formation of lepidocrocite and a mixture of
241 magnetite and maghemite, respectively.^{19,87}

242

243 **2.5. X-ray Absorption Spectroscopy (XAS)**

244 Despite the widespread use in the fields of geochemistry and material science, XAS has
245 had a limited application in NZVI studies with only a handful of studies describing the use of
246 this technique to characterization of NZVI^{15,33,88,89} or NZVI passivation byproducts.^{36,79,86,90–92}
247 One of the great strengths of Fe K-edge XAS is that it can provide quantitative insight into all
248 the iron minerals present. This is because the high energy of the Fe K-edge (7112 eV for

249 Fe(0)), allows for the entirety of the particles to be sampled by the beam. As an XAS
250 spectrum is a linear combination of its components, it can then be fitted with reference
251 material spectra in a linear least-squares fitting manner using software such as ATHENA.⁹³
252 As recommended elsewhere,⁶⁷ the choice of reference material spectra and the number of
253 components to fit sample spectra should be guided on evidence from complementary
254 analytical techniques, knowledge of the NZVI system, or principle component analysis and
255 target analysis.

256 In the NZVI studies mentioned above, either the X-ray absorption near-edge structure
257 (XANES) or extended X-ray absorption fine structure (EXAFS) regions of the XAS spectrum
258 have been modelled. Generally, the Fe K-edge XANES region can be used for fitting spectra
259 when there are multiple Fe oxidation states present.^{86,89-91} However, it is a less useful region
260 to distinguish between Fe(III) oxyhydroxide passivation byproducts. For example, the
261 XANES spectra of ferrihydrite, lepidocrocite and goethite can, for fitting purposes, be
262 practically identical when using a Si(111) monochromator. If the identity of the exact Fe(III)
263 oxyhydroxides is an important component of a NZVI study, then the EXAFS region is better
264 suited for fitting of data.^{36,92} Interestingly, all the XAS studies that have examined NZVI
265 passivation byproducts have done so under oxidative conditions. Nevertheless, as noted in
266 many other NZVI studies, lepidocrocite, magnetite and maghemite are the main secondary
267 iron minerals that have been detected by XAS analysis^{36,79,90-92} though ferrihydrite and
268 goethite have also been reported.^{36,79,92}

269

270 3. NZVI PASSIVATION PROCESSES UNDER ANOXIC AND OXIC CONDITIONS

271 In this section, we review the state of knowledge with regard to the mechanism of
272 passivation of NZVI under both anoxic and oxic conditions. Under anoxic conditions, the
273 reaction with water is expected to be of principal importance for the formation of passivating

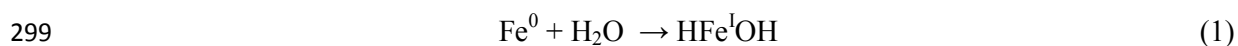
274 layers on the NZVI surface though attention is also given to the impact of other major
275 solution constituents (such as carbonate, sulfate and nitrate) that may be present. Under oxic
276 conditions, the presence of oxygen is obviously the major differentiator to anoxic systems
277 with O₂ potentially influencing the reaction pathway of Fe(II) resulting from NZVI corrosion.
278 Consideration is also given to the impact of the nature of the NZVI particle on the oxic
279 passivation process with bimetallic particles of major interest.

280

281 3.1. Anoxic Conditions

282 With respect to the anoxic reaction of NZVI with water, the identification of the
283 primary reductive products (particularly Fe(OH)₂ and magnetite) and the definition of the
284 reaction mechanism have been well addressed by Filip et al.³⁹ These investigators³⁹
285 used “NANO FER 25P” NZVI particles of ~60 nm in diameter and a specific surface area of
286 ~36 m²g⁻¹ that were thermally synthesized from iron oxide powder in H₂. Aging studies were
287 undertaken under strictly anoxic conditions at both 25 °C and 80 °C. ⁵⁷Fe Mossbauer
288 spectroscopy indicated that approximately 70% of the Fe(0) was transformed to Fe(OH)₂ after
289 ~3000 h of reaction at 25 °C with this mineral transforming relatively rapidly (after ~200 h) to
290 magnetite (Fe₃O₄) at 80 °C (Figure 2). Interestingly, the results obtained by Filip et al.³⁹ were
291 at odds with the results of earlier workers such as Reardon et al.⁹⁴ who concluded that
292 magnetite was also formed at 25 °C. Filip et al.³⁹ investigated this discrepancy and showed
293 that the nanosheets of Fe(OH)₂ formed in their study could be rapidly transformed to
294 magnetite on exposure to air during analysis by XRD – the solid characterization method used
295 by Reardon et al.⁹⁴. Quantum chemical calculations indicated a two-step reaction mechanism
296 involving two one electron transfer processes; the first, which involved the breakage of the H-
297 O bond of water, can be described by the reaction (Eq.1):

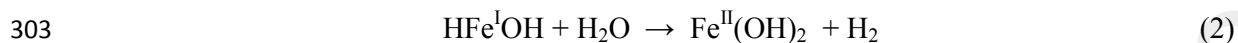
298



300

301 which represents the rate-limiting step, and the second by (Eq.2):

302



304

305 Filip et al.³⁹ note that the existence of the HFeOH molecule has previously been demonstrated
306 (by Zhang et al.⁹⁵) by argon matrix isolation FTIR spectroscopy.

307 The nature of the corrosion products formed on NZVI upon exposure to anoxic solutions
308 has been investigated in a more recent study with Liu et al.⁷⁸ concluding that the major
309 passivation byproducts formed after 72 h of reaction were wüstite ($\text{Fe}^{\text{II}}\text{O}$), goethite and
310 akageneite (Figure 3). These products differ markedly from those reported by Filip et al.³⁹ and
311 beg the question of whether air exposure during TEM, XRD and Raman analyses resulted in
312 transformation of the passivation products formed under anoxic conditions. Pullin et al.⁷⁹
313 investigated the nature of the passivation byproducts formed on exposure of NZVI to Milli-Q
314 water for periods of more than four weeks with the nature of the passivation byproducts
315 investigated by XAS. Amorphous passivation products (assigned as ferrihydrite) were formed
316 within one day of exposure with the concurrent formation of magnetite. Over periods of up to
317 four weeks, maghemite was observed to form with this oxide transforming slowly to “meta-
318 stable” lepidocrocite. Over longer periods (greater than four weeks), all NZVI transformed to
319 goethite with this iron oxide considered to be the likely “final state”

320 In summary, the anoxic corrosion of NZVI by water is dependent upon various factors,
321 such as reaction time and temperature, with the major corrosion products observed being
322 wüstite, goethite and magnetite. It should be recognized, however, that the intrusion of
323 oxygen either through the aging process or during analysis may confound the results of

324 experiments undertaken under supposed anoxic conditions. As such, investigators should pay
325 particular attention to the possibility of unintended NZVI passivation during studies under
326 anoxic conditions.

327

328 **3.2. Oxic Conditions**

329 The nature of the oxidation products formed on exposure of nanometer-sized Fe(0)
330 particles to oxygen has been of interest for many years in view of the widespread use of
331 ultrafine magnetic particles in magnetic recording, ferrofluids and catalysis with the nature of
332 the oxide phases formed on exposure of small iron particles to an oxygen-containing
333 atmosphere investigated by a number of groups.⁹⁶ Linderoth et al.⁹⁶ found, using Mössbauer
334 spectroscopy, that the oxide layer grows quickly initially then slows down with the oxide
335 layer consisting of a mixture of Fe₃O₄ and γ -Fe₂O₃. The kinetics of oxide layer formation
336 followed a logarithmic rate law in accord with the Cabrera-Mott model of oxidation⁹⁷ with
337 multistage steps including i) dissociative adsorption of O₂ at the metal surface, ii) oxidation of
338 surface metal ions, iii) incorporation of metal ions into the oxide layer, iv) diffusion of metal
339 ions in the oxide layer, and v) reaction of metal ions with oxygen ions with the diffusion of
340 metal ions in the oxide layer considered to be rate limiting.⁹⁸

341 In comparison with the logarithmic behavior of oxide layer growth revealed from
342 studies of passivation of iron particles in air, investigations of the oxidation of Fe(0) surfaces
343 in the presence of water vapour reveal that reactions at the iron surface/water interface are rate
344 limiting with an initial lag in oxide layer formation followed by an exponential increase in
345 growth of the oxide layer.⁹⁹⁻¹⁰¹ Investigation of the aging of iron nanoparticles in aqueous
346 solution by Sarathy et al.¹⁰² revealed similar behavior with Fe(0) nanoparticles from Toda
347 (RNIP-10DS) becoming more reactive (as determined by the rate of carbon tetrachloride
348 (CCl₄) reduction) between 0 and ~2 days after exposure to water then gradually losing

349 reactivity over the ensuing 100 days. These changes in reactivity were correlated with
350 evidence for destruction of an Fe(III) oxide film that initially covered the Fe(0) nanoparticles
351 with subsequent formation of a new passivating mixed valence Fe(II)-Fe(III) oxide shell.¹⁰²

352 Using quartz crystal microbalance measurements to quantify the rate of oxide layer
353 formation, Greenlee et al.¹⁰³ showed similar behavior to that observed by Sarathy et al.¹⁰² with
354 an initial lag in oxide layer formation following by an exponential increase in mass of this
355 layer (Region 1 in Figure S2). Decrease in water content of the solutions used (by replacing
356 water with ethanol) resulted in an increase in the lag period before oxidation commenced and
357 a decrease in the rate once oxidation had begun with these results confirming the critical role
358 of H₂O in destabilizing the passivating layer initially present. As shown in Figure S2, this
359 exponential increase in oxide layer growth was followed by a logarithmic decline in rate of
360 corrosion at later times (Region 2) with this behavior in accord with the Cabrera-Mott model
361 described above. Greenlee et al.¹⁰³ showed that NZVI oxidized primarily to lepidocrocite with
362 both carboxymethylcellulose (CMC) stabilizer and Ni slowing down the onset and extent of
363 NZVI oxidation. Dong et al.¹⁰⁴⁻¹⁰⁶ also showed that CMC and Ni slowed the aging of NZVI
364 with the major products of oxidation found to be magnetite and maghemite.

365 Recent studies of NZVI-mediated oxidation by He et al.³⁶ confirmed the results of
366 earlier studies by Joo et al.³⁰ that both Fe(II) and H₂O₂ are generated following 1 h exposure
367 of NZVI to oxygenated water at circumneutral pH. The solid Fe species resulting from
368 exposure of NZVI to oxygen were examined, as a function of exposure time, by EXAFS
369 spectroscopy.³⁶ Linear combination fitting of the EXAFS results indicated that NZVI
370 transformed to lepidocrocite via an intermediate ferrihydrite phase following exposure of
371 NZVI to oxygenated water with essentially all NZVI transformed to ferric oxyhydroxides
372 after two hours of exposure to the oxic aqueous environment (Figure 1d).³⁶

373 In summary, crystalline iron (oxyhydr)oxides such as lepidocrocite, maghemite and
374 magnetite appear to be the major products formed upon the oxic corrosion of NZVI.
375 Ferrihydrite may form initially but Fe(II)-catalyzed transformation to more crystalline forms
376 is likely to occur as a result of the high concentrations of surface-associated Fe(II) present.
377 The particular iron (oxyhydr)oxide formed is likely to be a function of the molar ratio of Fe(II)
378 to Fe(III) surface sites present with the relatively short lifetime of Fe(II) in these oxic systems
379 also influencing the extent of crystallization.

380

381 4. FACTORS INFLUENCING NZVI PASSIVATION

382 Most of the published literature to date has addressed the impact of synthesis
383 methods¹⁰⁷ and both organic and inorganic compounds^{4,33,80,108–117} on the reactivity of NZVI
384 with respect to target contaminants in the context of groundwater or wastewater remediation.
385 In these studies, variations in the kinetic rate constants or extents of degradation were used as
386 a means of assessing reactivity changes upon exposure to different cations or anions.
387 However, very few attempts have been made to determine the corrosion mechanism(s) and to
388 relate reactivity changes to the nature of the passivation byproducts formed¹⁰⁷ and the surfaces
389 exposed to co-occurring solutes.^{33,80}

390

391 4.1. Effect of Synthesis Methods

392 The elemental composition of NZVI can vary depending on the synthesis method
393 used,^{117,118} which may influence NZVI reactivity as well as the nature of the passivation
394 byproducts. In most cases, Fe reduction is mediated by NaBH₄ (NZVI^{BH}) or H₂ (NZVI^{H2})
395 (Table 1). The XPS results revealed that the NZVI^{H2} surfaces composed of Fe (37.9–50.9%),
396 O (44.2–52.9%), B (0%), Na (0.7–8.1%) and S (0.9–1.9%, possibly from the FeSO₄
397 precursor).¹⁰⁷ The surface of the NZVI^{BH} particles contained less Fe (20.0%–30.8%) and S

398 (0.0%–0.5%), but greater O (49.1–59.2%), B (12.0–16.0%) and Na (0.5–14.5%).^{107,118}
399 Moreover, it was found that the S on the NZVI^{BH} surface was in an oxidized form, whereas
400 the S present on the surface of the NZVI^{H2} particles was in reduced form.¹⁰⁷ Interestingly,
401 NZVI^{H2} exhibited lower reactivity than NZVI^{BH} for the transformation of CCl₄ to chloroform
402 (CHCl₃), presumably due to the high Fe/O ratio (possibly associated with the presence of a
403 magnetite shell) on the NZVI^{H2} surfaces.¹⁰⁷ This hypothesis was supported by the low ability
404 of nanoscale magnetite to transform CCl₄.¹¹⁹ These results serve to demonstrate that synthesis
405 methods could alter the surface reactivity of NZVI and potentially its passivation mechanism.

406 As noted above, the use of NaBH₄ during the synthesis of NZVI^{BH} can result in the
407 occurrence of B on the surface of NZVI^{BH}.¹²⁰ Recently, it has been reported that NaBH₄ can
408 induce the disintegration of NZVI^{BH} particles, resulting in the formation of significantly
409 smaller particles.¹²¹ This phenomenon may be induced by chemical etching of the passivated
410 NZVI surface (coated, for example, by iron oxides such as magnetite) with this result
411 consistent with the ability of NaBH₄ to induce the disintegration of microscale magnetite into
412 nanoscale magnetite.¹²² Although these authors did not compare their results to NZVI^{H2}, the
413 disparity in elemental surface composition (e.g., more Fe and S with less Na on the NZVI^{H2}
414 surfaces) may possibly cause reactions to proceed differently.

415

416 4.2. Effect of Inorganic Compounds

417 Although the corrosion rate of NZVI and the nature of the passivation byproducts can be
418 significantly affected by the presence of anionic or cationic inorganic species, very few
419 studies have focused on this topic.^{33,80} The corrosion phenomenon is dependent on several
420 factors including the type and concentration of aqueous species, reaction time and oxic/anoxic
421 environments.^{33,80} It has been reported that the presence of common groundwater anions may
422 promote or inhibit the corrosion of NZVI, however limited insight into the mechanism(s) of

423 the effects of anions is available.^{33,80} After six months of aging in pH unbuffered and anoxic
424 solutions containing 10 mM of either HCO_3^- , SO_4^{2-} , NO_3^- , HPO_4^{2-} or Cl^- , NZVI (commercial
425 sample, RNIP 10-DP) was found to predominantly transform to vivianite in the phosphate-
426 aged sample and schwertmannite in the sulfate-aged sample (Figure S3).³³ Both the fresh
427 NZVI and the sample aged for six months in 10 mM nitrate predominantly contained Fe(0)
428 and magnetite.³³ The pH of the suspensions containing the different anions ranged from 9.0–
429 11.8, indicating that the observed transformations occurred under alkaline conditions.³³ Using
430 the same concentrations of the anionic species, NZVI^{H2} particles have also been found to
431 undergo corrosion into different iron phases after 16 weeks.⁸⁰ For example, HCO_3^- produced
432 goethite, NO_3^- resulted in the formation of magnetite/maghemite and SO_4^{2-} and Cl^- produced
433 a mixture of magnetite/maghemite, lepidocrocite and goethite (Figure S4).⁸⁰ It was observed
434 that the corrosion rate of NZVI increased in the order $\text{HCO}_3^- > \text{Cl}^-/\text{SO}_4^{2-} > \text{NO}_3^-$, however
435 pH was only measured in experiments in which the uptake of Cu and Zn by the corroded
436 NZVI was examined over a time period of 4 weeks.⁸⁰ As such, the influence of this critical
437 parameter on the nature of the formed passivation byproducts is unknown. Elsewhere, Kim et
438 al.¹¹⁷ have reported that a commercial NZVI (NANO FER 25DS) coated by S-based inorganic
439 compounds was oxidized to magnetite in a synthetic groundwater containing Cl^- (1.95 mN),
440 HCO_3^- (1.14 mN), NO_3^- (0.15 mN) and SO_4^{2-} (0.44 mM). In contrast, iron carbonate hydroxide
441 hydrate was detected as a major passivation byproduct in the presence of humic acid (2.5 mg
442 L^{-1}).

443 Xie and Cwiertny⁴ have reported that the presence of Cl^- , SO_4^{2-} and ClO_4^- almost
444 completely inhibited the reduction of 1,1,1,2-tetrachloroethane by NZVI over a time period of
445 one month, irrespective of the nature or concentration of the anion present or pH. In contrast,
446 the longevity toward degrading this contaminant was dependent upon the concentrations of
447 NO_3^- and HCO_3^- with complete reactivity loss over 1 d and 14 d, respectively, in 25 mM

448 suspensions. In addition, XRD analyses suggested that the loss in reactivity in NO_3^-
449 suspensions resulted from $\text{Fe}(0)$ conversion into magnetite, whereas the formation of iron
450 carbonate hydroxide limited reactivity in the HCO_3^- suspensions (Figure 4). Furthermore, Liu
451 et al.¹⁰⁸ reported that trichloroethylene (TCE) reduction rates by NZVI are highly dependent
452 on anion concentrations. For example, concentrations below 1 mM NO_3^- slightly increased the
453 reduction rate but the reaction was retarded at NO_3^- concentrations between 1 and 3 mM and
454 ceased at 5 mM. It was speculated that high NO_3^- concentrations may shift the TCE reduction
455 reaction from one of cathodic control (i.e., the reduction of TCE) to anodic control (i.e., the
456 release of Fe^{2+} and electrons) resulting in significant surface passivation.

457 On the other hand, Su et al.¹⁰⁹ reported that the rate of degradation of hexachlorobenzene
458 by NZVI was not influenced by the presence of HCO_3^- , Mg^{2+} or Na^+ (over the concentration
459 range of 0.8–7.7 mM). However, the rate of degradation was enhanced in the presence of 7.7
460 mM Cl^- or SO_4^{2-} due to the promotion of corrosion but inhibited in the presence of 7.7 mM of
461 NO_3^- due to the competition between the anions and contaminants for reactive surface sites.
462 However, it has been observed that the addition of Na_2SO_4 inhibited the degradation of
463 pentachlorophenol (PCP) by Pd/Fe bimetallic nanoparticles in the range of 2.5–10 mM¹¹⁰ and
464 the decolorization of methyl orange by NZVI particles at 14 mM.¹¹¹ Researchers generally
465 attribute the inhibitory effects of common groundwater anions to their affinity for surface sites
466 on the iron (oxyhydr)oxides coating the NZVI with the resulting surface complexes limiting
467 the ability of contaminants to associate with the surface. Consistently, the inhibition effect has
468 been found to increase in the order of $\text{Cl}^- < \text{SO}_4^{2-} < \text{HPO}_4^{2-}$ for nitrate reduction by Peerless
469 $\text{Fe}(0)$ ¹¹² and $\text{Cl}^- < \text{SO}_4^{2-} < \text{HCO}_3^- < \text{HPO}_4^{2-}$ for TCE reduction by NZVI.¹⁰⁸

470 Given that the standard reduction potential of Na^+ ions (-2.71 V) is below that of Fe^{2+}
471 ions (-0.44 V), Na^+ ions do not affect degradation reactions mediated by $\text{Fe}(0)$.¹⁰⁹ However,
472 Cu^{2+} (0.8–7.7 mM) has been shown to enhance the degradation kinetics of hexachlorobenzene

473 by NZVI whereas Fe^{2+} (0.8–7.7 mM) has been reported to inhibit the degradation reaction due
474 to the formation of passivation layers on the particle surfaces.¹⁰⁹ Moreover, Cu^{2+} (5–10 mM),
475 Ni^{2+} (5–10 mM) and Fe^{3+} (1.67–5 mM) have been observed to enhance PCP degradation by
476 Pd/Fe nanoparticles due to the deposition of reduced copper and nickel species on the Fe
477 surfaces.¹¹⁰ The standard reduction potentials of the Cu^{2+} (+0.34 V) and Ni^{2+} (–0.257 V)
478 cations are significantly higher than that of Fe^{2+} (–0.44 V) and, as such, the reduction of Cu^{2+}
479 or Ni^{2+} ions to their elemental forms is thermodynamically favorable.^{113,114} In the case of the
480 Fe^{3+} cation, the enhancement observed in the PCP degradation was attributed to a decrease of
481 pH resulting from the addition of the iron salt.¹¹⁰ Furthermore, spectroscopic investigations of
482 the structural evolution of NZVI in anoxic Co^{2+} solutions revealed that Co^{2+} was
483 heterogeneously reduced ($E_0 = -0.28$ V) and migrated to the NZVI core leading to its
484 continuous removal from the solution.¹¹⁵ However, information on whether Co^{2+} affects the
485 nature of passivation byproducts is lacking though dissolution of sheet or shell structures upon
486 metal complexation on the Fe surface has been reported in depassivation studies of micro-
487 scale ZVI (~70 mesh) by Liu et al. (Figure 5).^{85,116}

488 In summary, anionic ligands such as phosphate, silicate and sulfate may be readily
489 adsorbed onto iron corrosion products, affecting the reactivity of NZVI particles. Hard cations
490 (such as Ca^{2+} and Mg^{2+}) and transition cationic metals (such as Ni^{2+} , Cu^{2+} and Co^{2+}) may
491 exhibit promotive or inhibitive effects depending on their properties. However, the main
492 secondary iron minerals formed during the reduction reaction have rarely been identified.

493

494 **4.3. Effect of Organic Compounds**

495 The use of organic ligands in NZVI studies has been investigated in the context of
496 colloidal stabilization to increase particle mobility and improve redox reactivity. For example,
497 chemical stabilizers (such as humic acid, polyacrylic acid and anionic or nonionic surfactants)

498 have been used to increase electrostatic repulsion effects and the stability of NZVI
499 particles.^{16,20,123,124} However, minimal attention has been given to the impact of stabilizers on
500 the passivation of NZVI.

501 In oxygenated solutions, NZVI can undergo four electron transfer steps leading to the
502 formation of reactive species such as HO^{*} and Fe(IV), which can potentially be utilized in the
503 oxidative degradation of certain organic contaminants. The addition of iron-chelating agents
504 such as oxalate, nitrilotriacetic acid, ethylenediaminetetraacetic acid, tetrapolyphosphate and
505 polyoxometalate may accelerate the formation of ROS by mediating electron transfer from
506 NZVI to oxygen (e.g., changing the four-electron transfer process to a two-electron transfer
507 process) and by forming soluble complexes with iron at neutral pH values.^{125–127} Although
508 these studies did not assess the NZVI passivation byproducts in the presence of iron
509 complexing agents and O₂, the acceleration of the NZVI corrosion rate is expected under such
510 conditions.

511 The effects of short chain organic acids (e.g., formic, oxalic and citric acid) on nitrate
512 reduction by Fe(0) has been observed to increase in accordance with the degree to which the
513 ligands adsorb to the surface of iron (oxyhydr)oxides or the stability constants of the aqueous
514 complexes between Fe(III) and the organic ligands.¹¹² The blockage of reactive sites on the
515 surface of Fe(0) and its passivation byproducts by the adsorption of ligands through an inner-
516 sphere complexation mechanism may be responsible for the observed decrease in reduction
517 rate. Unfortunately, information on whether and/or how the specific adsorption of ligands to
518 the outer layers of corrosion products may alter the ongoing passivation or structural
519 evolution of NZVI is very scarce.

520

521 5. DEPASSIVATION STRATEGIES

522 As discussed in the previous sections, most NZVI studies have focused on the
523 passivation of NZVI after its use in water decontamination reactions. A decrease in NZVI
524 reactivity is considered one of the major issues and a solution is required if NZVI is to be
525 used to effectively degrade contaminants. In this section, a variety of depassivation strategies
526 (including physical, chemical and biological approaches) are introduced to enhance and/or
527 prolong the reactivity of NZVI. Particular attention is given to the use of depassivation
528 strategies before, during and after the decontamination process.

529

530 **5.1. Depassivation before decontamination**

531 A well-known limitation to the broad application of NZVI for contaminant degradation is
532 rapid pyrophoric reaction in air and surface passivation in aqueous solutions. This has led to
533 studies examining possible synthesis procedures that can be used to produce reactive NZVI,
534 i.e., NZVI that is atmospherically stable⁸⁶ or stable in aqueous phase.¹²⁸ For example, the
535 shell-modified NZVI particles produced by Kim et al.⁸⁶ after controlled air-oxidation at
536 various flow rates for 1 d did not ignite upon later exposure to atmospheric conditions.
537 Shorter and longer controlled oxidation times resulted in spontaneous combustion or
538 significantly decreased TCE degradation rates, respectively.⁸⁶ The optimal shell-modified
539 NZVI particles exhibited a TCE degradation rate that was 78% of that obtained for fresh
540 NZVI (Figure S5). It was also revealed that after aging in water for 1 d, both the fresh and
541 shell-modified NZVI exhibited similar TCE degradation rate constants. It was conjectured
542 that surface depassivation of the shell-modified particles was the cause for this observation,
543 however, no mechanisms were examined or postulated.

544 It has been reported that annealing can induce structural and chemical changes in NZVI,
545 with re-ordering and recrystallization of the inner Fe core, so as to eliminate defects and
546 impurities.¹²⁹ In this case, the thickness of the surface oxide layer decreased from 3–4 nm to 2

547 nm by vacuum annealing at 500 °C with an accompanying change of the surface oxide from
548 magnetite to wüstite and the migration of boron and carbon to the particle surface.¹²⁹ This
549 depassivation process was postulated to improve the corrosion resistance and reactive lifespan
550 of NZVI for environmental applications. A subsequent study performed by this group
551 revealed that NZVI reactivity was significantly enhanced (by a factor of 30), with respect to
552 the degradation of TCE and cis-1,2-dichloroethene, when compared to that of fresh NZVI due
553 to efficient electron transfer from Fe(0) to the contaminants.¹³⁰

554 In recent years there has been an explosion of interest in the sulfidation of NZVI during
555 its synthesis to prevent surface passivation reactions that result from the reduction of water.
556 Using variations of the method first outlined by Kim et al.,¹²⁸ several studies have revealed
557 that sulfidated NZVI is superior to NZVI in decontamination reactions.^{35,128,131} Enhanced
558 decontamination by sulfidated NZVI has been hypothesized to result from the inhibition of
559 corrosion in water.⁶⁵ The formation of nanocrystalline FeS phases on the surfaces of
560 sulfidated NZVI, resulting in a high surface area and good electrical conductivity, has been
561 suggested to be responsible for the high reactivity of these nanoparticles toward contaminants
562 (Figure S6).¹²⁸ From a molecular point of view, dechlorination by reductive elimination may
563 be favored over hydrogenolysis as a result of sulfidation.⁶⁵ In addition, the surface of
564 sulfidated NZVI may act as a more efficient conductor of electrons from the inner Fe(0) to the
565 surface layers than iron (oxyhydr)oxides.^{131,132} Two recent review papers have highlighted
566 progress made in this research area.^{65,133}

567

568 **5.2. Depassivation during/after decontamination**

569 A significant amount of effort has been expended on the investigation of methods to
570 extend the longevity of NZVI during the removal of environmental contaminants. For
571 example, Bae and Lee⁸ recently demonstrated that an endogenous electron shuttle (i.e.,

572 riboflavin) can enhance the long-term dechlorination of CCl_4 by NZVI. Results from TEM
573 surface analyses revealed the removal of the passivated layer (Figure S7), presumably due to
574 reductive dissolution by riboflavin, which could result in an increase in the rate of electron
575 transfer. In addition, Wang et al.¹⁴ revealed that the addition of humic acid enhanced the rate
576 and extent of 4-chlorobiphenyl degradation by NZVI, given that the humic acid acted as an
577 electron shuttle, thus leading to the rapid transfer of electrons from NZVI to the contaminant.
578 Although the investigators did not investigate the depassivation of NZVI,^{8,14} their
579 experimental results indicated that other electron shuttles such as quinone moieties (e.g., *p*-
580 hydroquinone, lawsone, 9,10-anthraquinone-2,6-disulfonate (AQDS), etc.) may also lead to
581 an increase in the longevity of NZVI.

582 Ultrasound has commonly been used to improve the dispersivity and stability of NZVI
583 during decontamination of wastewater.^{134,135} This process induces cavitation leading to
584 extremely high local temperatures (up to 10000 K) and pressures (up to 5000 bar).¹³⁶ This can
585 cause pitting and cracking at particle surfaces resulting in the removal of the passivated
586 surface (oxyhydr)oxide layer.¹³⁷ The enhanced removal of several elements, including Zn^{2+} ,
587 Pb^{2+} and Cu^{2+} has been observed following the application of ultrasound with the increased
588 removal due probably to the removal of the passivated layer.¹³⁶

589 There have been very few studies on the regeneration of passivated NZVI after
590 decontamination¹³⁸ although several studies have been conducted on ZVI.^{85,116,139} Due to the
591 different Fe (oxyhydr)oxides that may form on corrosion of NZVI and ZVI and the inherent
592 physical and chemical differences of these particles, it is not appropriate to necessarily
593 assume similar mechanistic processes are operative for ZVI and NZVI. For example, a
594 significant enhancement of TCE reduction was observed when an iron reducing bacteria
595 (*Shewanella putrefaciens*) was inoculated into a passivated ZVI suspension but not when
596 introduced to NZVI.¹³⁸ It was speculated that the biologically-mediated reductive dissolution

597 of the passivating layer re-exposed the ZVI Fe(0) core whereas a minimal amount of Fe(0)
598 was conserved in the case of passivated NZVI. Overall, the lack of studies on NZVI
599 depassivation after decontamination reactions is a result of the small size and highly reactive
600 nature of NZVI, which generally leads to its rapid transformation to Fe(II) and Fe(III)
601 minerals.

602

603 **6. ENVIRONMENTAL SIGNIFICANCE AND FUTURE APPLICATIONS**

604 NZVI has been one of the most intensively studied nanomaterials in environmental
605 engineering over the past 20 years, particularly in relation to its potential use in remediating
606 soil, groundwater and wastewater. Despite the extensive *in situ* and *ex-situ* use of NZVI for
607 contaminant removal, rapid surface passivation resulting in loss of NZVI reactivity is
608 considered one of the most severe problems with regard to its effective application. As
609 discussed in this review, the nature and extent of NZVI passivation may differ markedly
610 depending on the particular conditions in which NZVI is applied (Figure 6). As such, the need
611 exists to investigate the particular passivation mechanism, the factors that influence the rate
612 and extent of passivation and possible depassivation techniques suited to promoting the
613 efficacy of NZVI for each proposed application.

614 Most of the published literature to date has investigated the reactivity of NZVI with very
615 little attention paid to its passivation mechanisms. The reaction between NZVI and
616 contaminants is generally used to assess particle reactivity, however analyses of NZVI
617 transformations have rarely been conducted by investigators. Moreover, passivation effects
618 are more significant when NZVI is applied at a pilot- and/or field-scale due to the presence of
619 many influencing factors (e.g., long reaction time, O₂ levels, presence of inorganic and
620 organic contaminants and biotic influences). A systematic analysis of the effects of

621 passivation is therefore necessary to provide a comprehensive understanding of NZVI
622 chemistry during long-term applications (e.g., groundwater and soil remediation).

623 In this review, the most recent information with respect to the characterization techniques
624 for identifying passivation mechanisms have been summarized, in addition to important
625 factors that influence depassivation under different O₂ conditions and thereby extend the
626 longevity of NZVI. It becomes clear that there are significant challenges to overcome to
627 further advance NZVI as a remedial agent for environmental pollution. These challenges
628 include: (i) the establishment of advanced time-resolved methodologies to monitor NZVI
629 transformations; (ii) the evaluation of the contribution of passivation byproducts to sequential
630 contaminant removal; (iii) the investigation of microbial populations promoted by the
631 passivation byproducts after soil and groundwater remediation and (iv) the development of
632 novel and efficient depassivation strategies during and after NZVI application.

633 In engineered systems (such as wastewater treatment), the assessment of NZVI corrosion
634 byproducts and depassivation ways in order to improve and/or maintain contaminant removal
635 performance will be critical for developing a cost-effective NZVI-based technologies and
636 designing large-scale applications. In natural systems (such as soil and groundwater
637 environments) where nanoparticles are injected into affected zones, a comprehensive
638 examination of the transformation and mobility of the injected nanoparticles is essential for
639 ecological risk assessments. This will improve our ability to develop new simulation tools for
640 accurately predicting the overall performance of NZVI-based technologies as well as the fate
641 of NZVI particles in natural systems.

642

643 **ASSOCIATED CONTENT**

644 **Supporting Information**

645 The Supporting Information is available free of charge via on the ACS publications websites
646 at DOI:

647 Figures S1 to S7 (PDF).

648

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653

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Table 1. Representative studies reporting passivation byproducts of NZVI under different experimental conditions.

Synthesis method	Reaction condition	O ₂ condition	Reaction time	Passivation byproduct	Refs
Fe ³⁺ + NaBH ₄	complete mixing	oxygenated water	3 d	Lepi	38
		+ oxic condition			
FeCl ₃ ·6H ₂ O + NaBH ₄	no mixing	oxygenated water	5 d	Magn/Magh	77
		+ oxic condition	10 d	Ferr/ Magn/Magh	
			90 d	Lepi	
Fe ₂ (SO ₄) ₃ ·6H ₂ O + NaBH ₄	Cl ⁻ (10 mM)	water	2 h	Magn/Magh	80
		+ oxic condition	2 w	Akag/ Magn/Magh	
			16 w	Lepi /Magn/Magh	
Fe ₂ (SO ₄) ₃ ·6H ₂ O + NaBH ₄	HCO ₃ ⁻ (10 mM)	water	2 h	Magn/Magh	80
		+ oxic condition	8 w	Goet/ Magn/Magh	
Fe ₂ (SO ₄) ₃ ·6H ₂ O + NaBH ₄	NO ₃ ⁻ (10 mM)	water	2 h	Magn/Magh	80
		+ oxic condition	16 h	Magn/Magh	
Fe ₂ (SO ₄) ₃ ·6H ₂ O + NaBH ₄	SO ₄ ²⁻ (10 mM)	water	2 h	Magn/Magh	80
		+ oxic condition	2 w	Lepi/Magn/Magh	
			16 w	Goet/Lepi/Magn/Magh	

RNIP 10-DP, product from Toda Kogyo Corp., Reduction of Fe(III) oxides by H ₂	NO ₃ ⁻ (10 mM) + rotated end-over-end at 22 °C	deaerated water + anoxic condition	6 m	Magn	33
RNIP 10-DP, product from Toda Kogyo Corp., Reduction of Fe(III) oxides by H ₂	PO ₄ ²⁻ (10 mM) + rotated end-over-end at 22 °C	deaerated water + anoxic condition	1 m 6 m	Magn Vivi/Schw	33
NANOFER 25DS, product from NANO IRON (inorganic S based coating), Reduction of Fe(III) oxides by H ₂	Synthetic groundwater (Cl ⁻ (1.95 mN), HCO ₃ ⁻ (1.14 mN), NO ₃ ⁻ (0.15 mN), SO ₄ ²⁻ (0.44 mM))	deaerated water + anoxic condition		Magn	117
NANOFER 25 DS, product from NANO IRON (inorganic S based coating), Reduction of Fe(III) oxides by H ₂	Synthetic groundwater (Cl ⁻ (1.95 mN), HCO ₃ ⁻ (1.14 mN), NO ₃ ⁻ (0.15 mN), SO ₄ ²⁻ (0.44 mM)) + Humic acid (2.5 mg L ⁻¹)	deaerated water + anoxic condition		Iron carbonate hydroxide hydrate	117
FeCl ₃ •6H ₂ O + NaBH ₄	microcystin-LR (5.0 mg L ⁻¹) + PO ₄ ²⁻ (0.4 mM) + added H ₂ O ₂ (6.6 mM)	water + oxic condition	4 h	Vivi	34
FeCl ₃ •6H ₂ O + NaBH ₄	microcystin-LR (5.0 mg L ⁻¹) + humic acid (0.4 mM) + added H ₂ O ₂ (6.6 mM)	water + oxic condition	4 h	Lepi	34

$\text{FeCl}_3 \cdot 6\text{H}_2\text{O} + \text{NaBH}_4$	microcystin-LR (5.0 mg L^{-1}) + oxalate (0.4 mM) + added H_2O_2 (6.6 mM)	water + oxic condition	4 h	Magn/Lepi	34
NANOFER STAR, product from NANO IRON	synthetic groundwater with an ionic strength of 15 mM	groundwater + anoxic condition	6 d	Amak/Goet/Magn	81
$\text{Fe}^{3+} + \text{NaBH}_4$	As(V) (2 mg L^{-1}) + synthetic groundwater at pH 5	groundwater + oxic condition	30 d 60 d	Magn/Magh/Lepi/Hema Lepi	18
$\text{Fe}^{3+} + \text{NaBH}_4$	synthetic groundwater at pH 9	groundwater 1 IU+ oxic condition	30 d 60 d	Magn/Magh Magn/Magh	18
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O} + \text{NaBH}_4$	U(VI):Fe(0)=1:21, 50 mM NaCl , 5.8 mM NaHCO_3 and 1 mM CaCl_2 , synthetic groundwater at pH 7	groundwater + anoxic condition	3 d 12 m	Chuk Chuk/Magn	82
$\text{FeCl}_3 \cdot 6\text{H}_2\text{O} + \text{NaBH}_4$	NO_3^- (100 mg L^{-1}), HCO_3^- (5 g L^{-1})	deaerated water + anoxic condition	3 h	Gree(CO_3)	83
$\text{FeCl}_3 \cdot 6\text{H}_2\text{O} + \text{NaBH}_4$	NO_3^- (100 mg L^{-1}), Humic acid (1 g L^{-1} ; DOC = 320 mg L^{-1})	deaerated water + anoxic condition	3 h	Magn	83
$\text{FeCl}_3 \cdot 6\text{H}_2\text{O} + \text{NaBH}_4$	complete mixing at 300 rpm	deaerated water + anoxic condition	3 d	Wust/Goet/Lepi	78

FeSO ₄ •7H ₂ O + NaBH ₄ + carboxymethyl cellulose	Na ₂ S ₂ O ₄ (0.1 M), rolling on a hematology mixer at 15 rpm and pH 7.2	deaerated water + anoxic condition	2 d	Mack	35
FeCl ₂ •4H ₂ O + NaBH ₄	1 μM H ¹⁴ COO ⁻ , pH 6.2–8.3	oxygenated water + oxic condition	1 d	Side	36
RNIP 10-DS, product from Toda America, Inc. Reduction of Fe(III) oxides by H ₂	Dry powder	deaerated water + anoxic condition	<20 d	Mixed-valent Fe(II) and Fe(III) oxide	102
RNIP 10-DP, product from Toda Kogyo Corp. Reduction of Fe(III) oxides by H ₂	Alkaline slurry, pH =10.6	deaerated water + anoxic	2 y	Magn	140

Lepi: Lepidocrocite (γ -Fe^{III}OOH), Magn: Magnetite ($\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}_2\text{O}_4$), Magh: Maghemite (γ -Fe^{III}₂O₃), Ferr: Ferrihydrite ($5\text{Fe}^{\text{III}}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$), Akag: akageneite (β -Fe^{III}OOH), Schw: schwertmannite ($\text{Fe}^{\text{III}}_{16}\text{O}_{16}(\text{OH},\text{SO}_4)_{12-13} \cdot 10-12\text{H}_2\text{O}$), Wust: wüstite (Fe^{II}O), Amak: amakinite (Fe^{II}(OH)₂), Goet: goethite (α -Fe^{III}OOH), Hema: hematite (α -Fe^{III}₂O₃), Vivi: vivianite (Fe^{II}₃(PO₄)₂•8H₂O), Gree(CO₃): Carbonate green rust: [Fe^{II}₄Fe^{III}₂(OH)₁₂][CO₂•H₂O], Mack: mackinawite (Fe^{II}S), Side: siderite (Fe^{II}CO₃)

Figure captions

Figure 1. STEM images and XEDS maps showing NZVI oxidation by oxygen-containing water (a) fresh NZVI, (b) after 30 min and (c) 5 h reaction. (d) The corresponding graph shows the proportions of Fe present as either Fe(0), ferrihydrite or lepidocrocite as determined by linear combination fitting of EXAFS data. Reproduced with permission from ref 36, Copyright 2016, American Chemical Society.

Figure 2. TEM images of NZVI after reaction with water under anoxic conditions at (a) 25 and (b) 80 °C, respectively, and the long-term corrosion results at (c) 25 and (d) 80 °C, showing the proportions of Fe present as either Fe(0), Fe(OH)₂, or magnetite as determined by ⁵⁷Fe Mössbauer Spectroscopy. Reproduced with permission from ref 39, Copyright 2014, American Chemical Society.

Figure 3. A conceptual model on the passivation of NZVI in water showing that the main passivation byproducts include wustite (FeO), goethite (α -FeOOH) and akaganeite (β -FeOOH) under anoxic conditions while crystalline lepidocrocite (γ -FeOOH) with acicular-shaped structures forms under oxic conditions. Reproduced with permission from ref 78, Copyright 2017, Elsevier.

Figure 4. Results of TEM (a and c) and XRD (b and d) of NZVI showing the passivation of NZVI over one month at pH 8 in 5 and 25 mM HCO₃⁻ suspensions. The XRD diffraction patterns associated with specific mineral phases are noted as α -Fe for Fe(0), M for magnetite, GR for carbonate green rust, and ICH for iron carbonate hydroxide. Reproduced with permission from ref 4, Copyright 2012, American Chemical Society.

Figure 5. Schematic illustration showing the cation-induced depassivation process of aged micro-scale ZVI by Fe(II) dissolution of sheet or shell structures upon metal complexation on the NZVI surface. Cations: M^{2+} : Ba^{2+} , Sr^{2+} , Ca^{2+} , Mg^{2+} , Mn^{2+} , Co^{2+} , Fe^{2+} , Ni^{2+} , Zn^{2+} , Pb^{2+} , and Cu^{2+} . Reproduced with permission from ref 85, Copyright 2014, American Chemical Society.

Figure 6. Schematic illustrations showing the NZVI applications, typical passivation process of NZVI at different conditions, and environmental significance of the passivation.

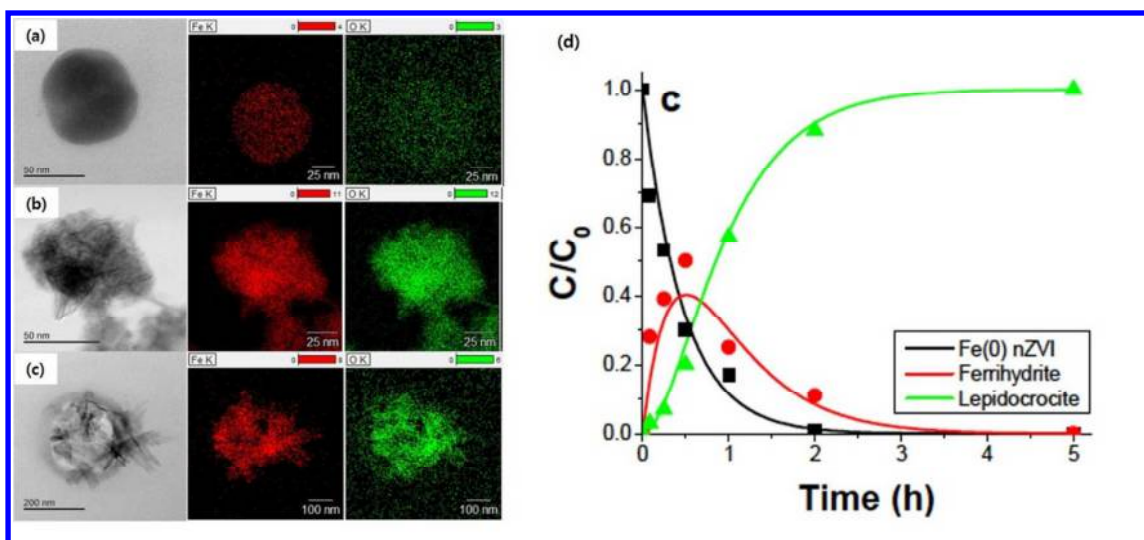


Figure 1.

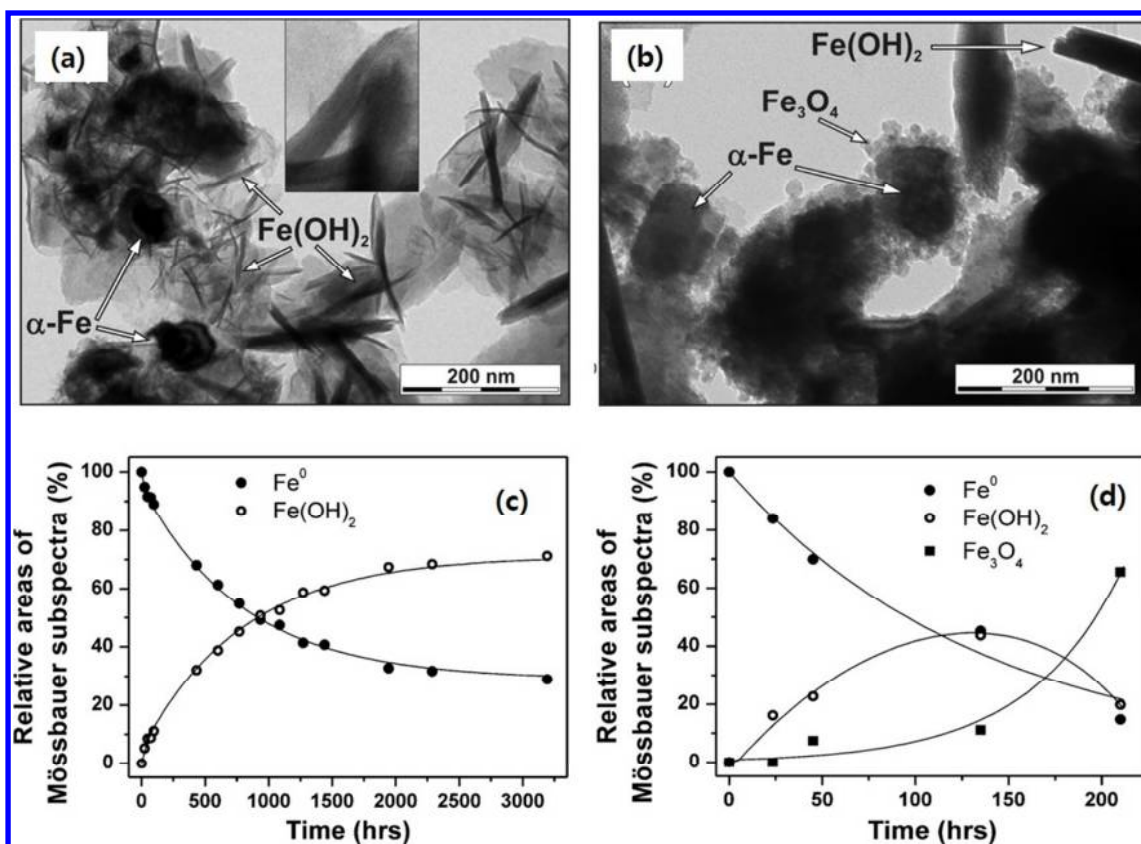


Figure 2.

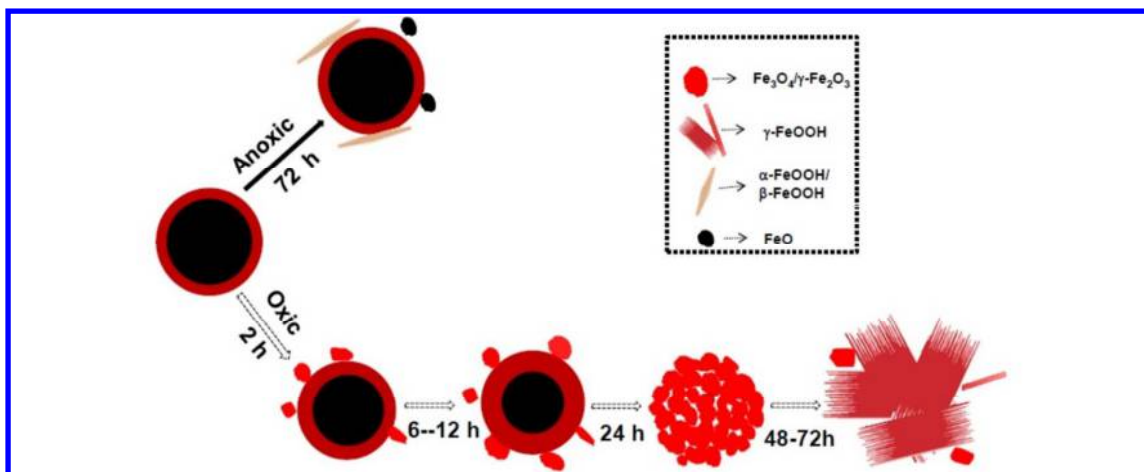


Figure 3.

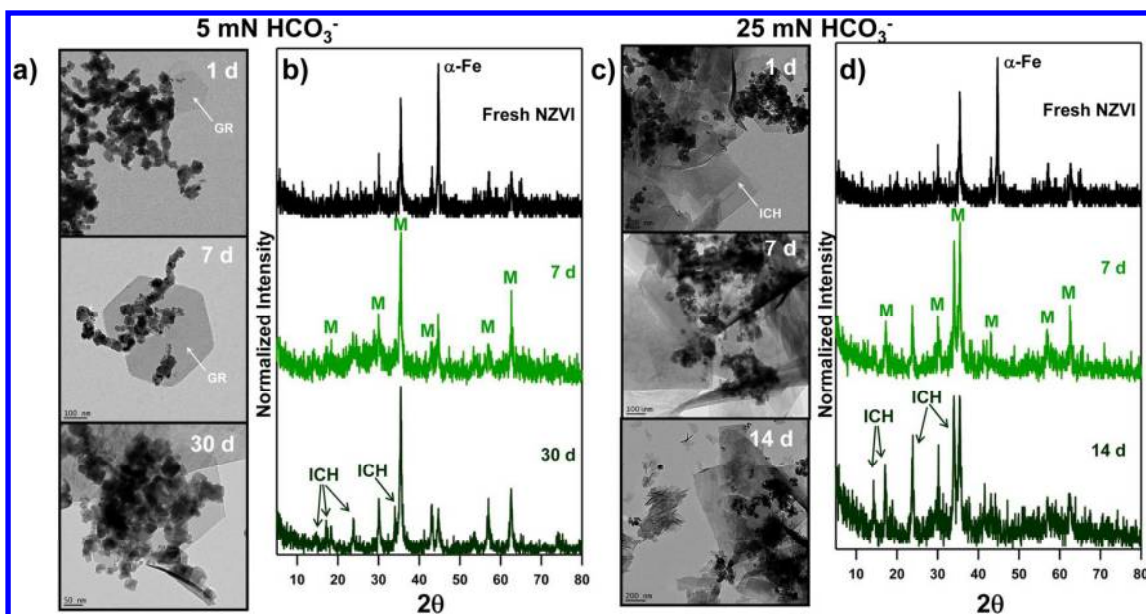


Figure 4.

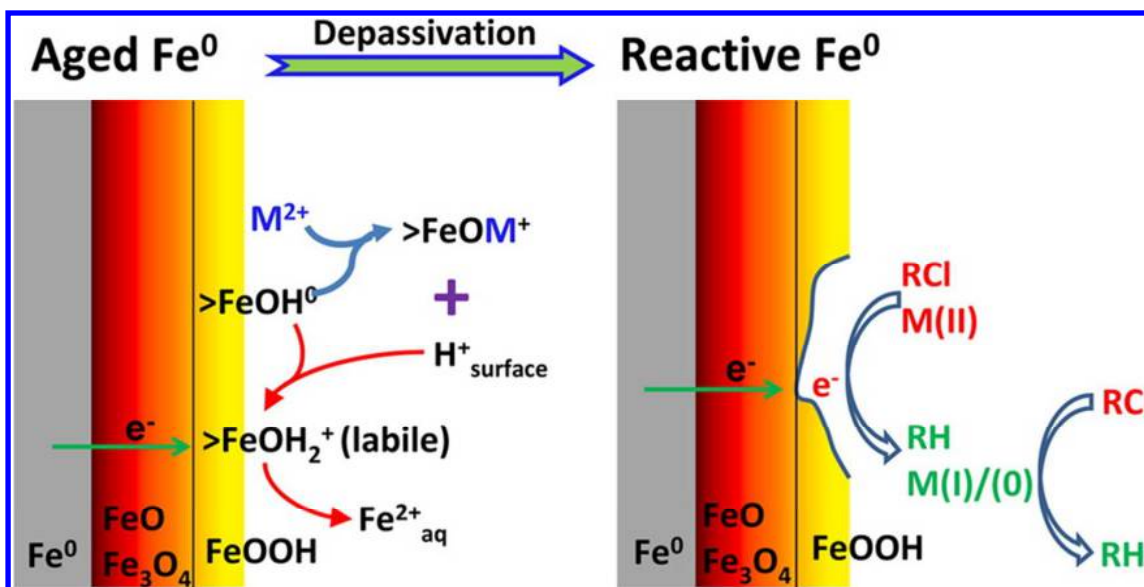


Figure 5.

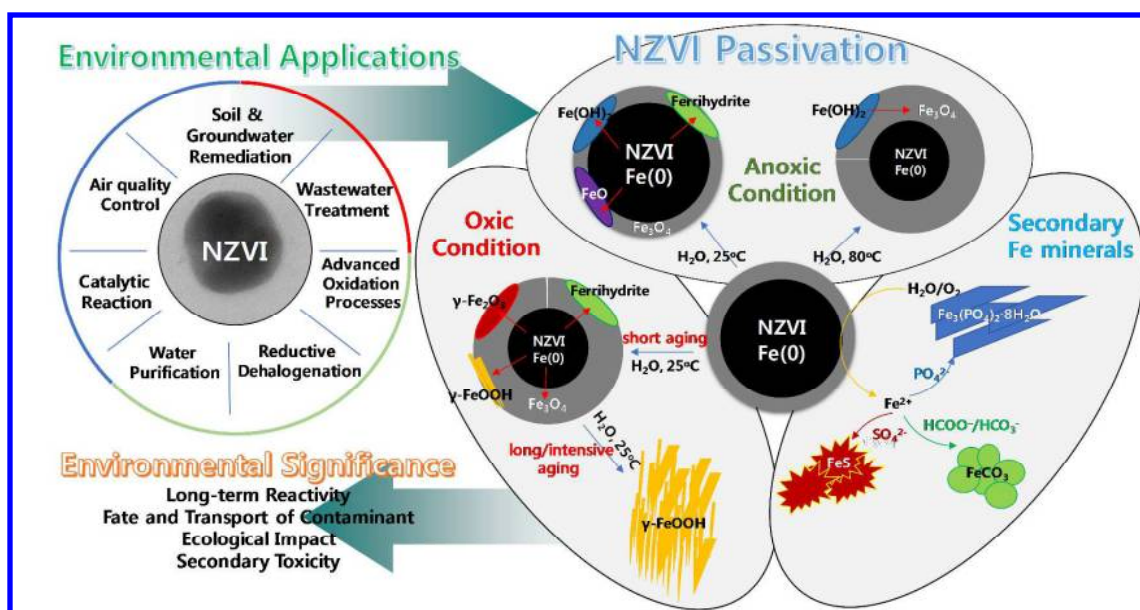
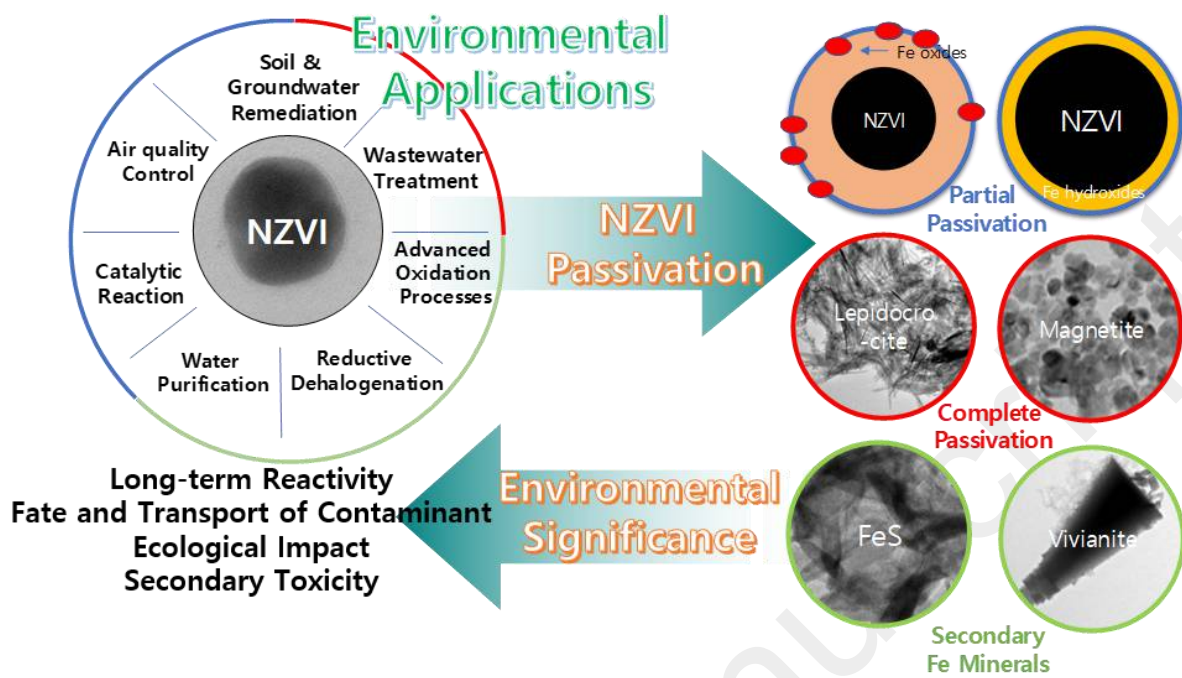


Figure 6.

TOC



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