The Suitability of Metallic Iron for Environmental Remediation

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Abstract

Aqueous contaminant removal in the presence of metallic iron is often regarded as a reductive transformation mediated by the Fe\(^0\) surface. However, successful removal of theoretically non-reducible contaminants has been largely reported. This paper presents a rebuttal of the concept of contaminant reductive transformation. It is argued through a careful examination of the evolution of the volume and adsorptive properties of iron and its corrosion products that contaminants are primarily adsorbed and co-precipitated with iron corrosion products. One may wonder how the Fe\(^0\) technology will develop with the new concept.

Keywords: Adsorption, Co-precipitation, Contaminant, Removal, Zerovalent iron.

Introduction

In 1990 Canadian hydrogeologists have rediscovered iron corrosion as metallic iron (Fe\(^0\)) became a remediation agent for contaminated aquifers, soils and waters. It was fortuitously found that Fe\(^0\) eliminated trichloroethylene from aqueous solutions (1-3). Since then intensive efforts have been devoted to remediation with Fe\(^0\) materials. As result Fe\(^0\) is now regarded as a very competent reactive agent for remediation of systems that are contaminated with reducible substances (including chlorinated hydrocarbons, nitrate, nitro aromatics, chromium, uranium) (4-8).

The rediscovery of iron corrosion was followed by a seminal work on the mechanism of aqueous contaminant removal in the presence of Fe\(^0\) (e.g. in Fe\(^0\)/H\(_2\)O systems) (9). These authors proposed three possible mechanisms for contaminant removal: (i) contaminant adsorption onto the surface of in situ formed corrosion products, (ii) contaminant reduction by...
Fe⁰ (direct reduction), (iii) contaminant reduction by FeII or H₂/H (indirect reduction). The work of Matheson and Tratnyek (9) was re-evaluated by Weber (10) and the results indicate that (i) direct reduction (electrons from Fe⁰) is the major reaction pathway, and (ii) reductive transformation by Fe⁰ is a surface-mediated process. Accordingly, the involved contaminant must contact the Fe⁰ surface for electron transfer to take place. Alternatively, the oxide film on Fe⁰ must be electronic conductive or the system must contain appropriate electron mediators (so-called “electron shuttles”). Since the work of Weber (10) the know-why of contaminant removal in Fe⁰/H₂O systems was considered to be achieved and the iron/sand mixture lost his nickname of “magic sand” (2). However, the acceptance of the concept of reductive transformation was primarily a consensus (4) as this concept failed to consistently explained many experimental facts (11-14). For example, while using differential pulse polarography to investigate the reduction of nitrobenzene in Fe⁰/H₂O systems, Lavine et al. (11) concluded that their studies were very informative but they couldn't evidence reduction of organic compounds as mediated by the Fe⁰ surface. Similarly, a very recent work of Jiao et al. (14) has shown that the reduction of carbon tetrachloride in the presence of Fe⁰ is primarily mediated by H₂ from iron corrosion (indirect reduction). Moreover, the quantitative removal for non-reducible species as methylene blue (15), triazoles (16) and zinc (17) in Fe⁰/H₂O systems has been reported. Because of the inconsistency of the consensus on the mechanism of contaminant removal in Fe⁰/H₂O systems, it was pertinent to reconsider the Fe⁰/H₂O system as a whole. For this purpose it is necessary to go back to the literature on metal corrosion.

**Fundamental aspects of aqueous metal corrosion**

Most metals (M) in their natural state are not pure metals (M⁰), but are in the form of metallic salts (mostly oxides - MₓOᵧ, sulphides - MₓSᵧ, and carbonates - Mₓ(CO₃)y). When these metal ores are refined or smelted, a losing battle with thermodynamics begins with the metal tending toward formation of metallic oxides, sulphides or carbonates depending on the
working environment (18-20). The rate and the extent at which a metal dissolves in an
aqueous environment (immersed metal corrosion) depends on many inter-dependant factors
(18, 21, 22) including: (i) the chemistry of water (pH, salinity, concentration and
concentration of chelating agents), (ii) the nature of the oxide layer formed by initial metal
corrosion (composition, electronic conductivity, porosity and thickness), (iii) the
manufacturing history of the metal (e.g. whether the metal been cast, forged, wrought or
welded), and (iv) the metal thermodynamic susceptibility to oxidation (position on the
reduction-potential scale). It has been established that the most important factor responsible
for immersed metal corrosion under conditions pertinent to natural waters (4.5 \( \leq \) pH \( \leq \) 9.5) is
the electronic conductivity and the porosity of the oxide layer (23). This statement will be
supported by a classical example.

Aluminium (\( E^0 = -1.71 \text{ V} \)) is more susceptible to oxidation than iron (\( E^0 = -0.44 \text{ V} \)) but Al is
known to be relatively inert to atmospheric and aqueous corrosion, whereas Fe is very
corrosive. There are two main reasons for this.

First, the oxidation of Al\(^0\) exclusively yields a non-conductive layer of Al\(_2\)O\(_3\) whereas the
oxidation of Fe\(^0\) may yield a conductive layer of Fe\(_{\text{II}}\)/Fe\(_{\text{III}}\) species (e.g. Fe\(_3\)O\(_4\), green rust) (24).
Accordingly an oxide film on Fe\(^0\) may act as a semiconductor and mediate electron transfer
from Fe\(^0\) (25-27). In this situation Fe\(^0\) corrosion continues despite the presence of the oxide
film. It is evident, that this behaviour can not be observed under oxic conditions where Fe\(_{\text{II}}\) is
instable and (at least) the outer layer of the oxide film will exclusively consist of non-
conductive Fe\(_{\text{III}}\) oxides (FeOOH or Fe\(_2\)O\(_3\)).

Second, the unit-cell in Al and Al\(_2\)O\(_3\) are very similar to one another; thus the aluminium
oxide can adhere tightly to the metallic aluminium beneath it (23). The oxidized surface
provides a protective layer that prevents oxygen from getting to the underlying Al surface. In
contrast, the packing dimensions of Fe\(^0\) and Fe oxides are not particularly close; thus there is
no tendency for an iron oxide layer to adhere to metallic iron. Therefore, regarding its
protective properties for iron corrosion, the “curse of rust” (23) is not that it forms, but that it constantly flakes off and exposes fresh iron surface for attack (23, 24). This “curse” of rust became a “blessing” in using Fe$^{0}$ for environmental remediation.

**Metallic iron for environmental remediation**

Fe-based alloys (Fe$^{0}$ materials, mostly cast iron and steel) are certainly suitable for environmental remediation because of their low tendency to passivity due to the porosity and the instability of generated oxide layers. Instead of this trivial reason, Fe$^{0}$ has been considered as a strong reducing agent for the reductive transformation of several species in natural waters (3-10). This consideration is not acceptable even from a pure thermodynamic perspective as the electrode potential of iron is almost the same (about -0.44 V) in low alloyed and stainless steels (Fe-based alloys). Accordingly, various Fe$^{0}$ materials should have exhibited similar behaviour for the removal of the same species. This has not been the case as for example Miehr et al. (28) reported variation of rate constants for contaminant removal varying over up to four orders of magnitude due to differences in Fe$^{0}$ “type”.

Because Fe$^{0}$ materials for environmental remediation are primarily susceptible to oxidation, complete passivation can only result from the transformation of initially non-protective films to impervious layers under specific environmental conditions. Therefore, a sake for an overview of factors likely to influence film formation and transformation (stability and breakdown) under environmental conditions should be undertaken. This could be a very difficult task because chemical breakdown occurs when the film is dissolved (e.g. by a chelating agent) or penetrated chemically (e.g. by a contaminant or Cl ions).

**Fundamental aspects of contaminant removal in Fe$^{0}$/H$_{2}$O systems**

While considering Fe$^{0}$ as a reducing agent for contaminant reductive transformation it has been impossible to explain several experimental and field observations as recalled above (also see refs. 29 and 30). The main reason for this is that iron corrosion products (oxide film) have been regarded as simple coatings, mediating at most electron transfer from Fe$^{0}$ to the
contaminant. However, the oxide film formation and transformation (recrystallization, dissolution, precipitation) is a dynamic process occurring in the presence of contaminants. Moreover, the oxide film formation can be regarded as the process of iron precipitation (31-33). Here, iron precipitation occurs in the presence of small amounts of foreign species (including contaminants). These foreign species are necessarily sequestrated within the oxide film as discussed in the next section (34). In this manner contaminants are primarily removed from the aqueous phase by a non-specific mechanism as they are just sequestrated in the matrix of precipitating iron oxides (33). This process is widely used in water treatment by electrocoagulation using Fe electrodes (Fe$^0$ EC) (35, 36) and explains why bacteria, viruses and thermodynamically non-reducible substances (e.g. Zn) have been quantitatively removed in Fe$^0$/H$_2$O systems. There are two main differences between passive Fe$^0$/H$_2$O systems and iron electrocoagulation: (i) Fe$^0$ oxidation is electrically accelerated in Fe$^0$ EC as the aim is to quantitatively produce iron hydroxides for contaminant removal by flocculation, and (ii) while contaminants are flocculated from the bulk solution in Fe$^0$ EC, they are precipitated in the vicinity of Fe$^0$ in passive Fe$^0$/H$_2$O systems. Accordingly a passive Fe$^0$/H$_2$O system could be regarded as a filter (working on the principle of size exclusion) in which species are additionally trapped by in situ generated iron hydroxides (and oxides).

It should be explicitly stated that adsorption, co-precipitation and redox transformations are not each other exclusive as adsorbed or co-precipitated contaminants may be further (i) reduced by Fe$^0$, adsorbed or soluble Fe$^{II}$ species or (ii) oxidized by HO$^\bullet$/H$_2$O$_2$ species (Fenton-like reactions). It is however certain, that the extend of reduction is difficult to evaluate. This assertion is supported by the fact that to date, no carbon balances between reactants and supposedly reaction products have ever been successfully done for many chlorinated hydrocarbons (3). However, one should no care about the fate of co-precipitated contaminants as they will remain sequestrated so far iron oxides are not dissolved. Alternatively and complementary, the possibility of iron oxide dissolution and its
consequence for co-precipitated contaminants should be discussed at each relevant site. The
next section will discuss on the suitability of the Fe\(^0\)/H\(_2\)O system for contaminant removal.

**Peculiarity of the Fe\(^0\)/H\(_2\)O system**

The singularity of the Fe\(^0\)/H\(_2\)O system is the in situ generation of soluble Fe\(^{II}\) species and their
further transformations to crystalline iron oxides and hydroxides (Fe(OH)\(_2\), Fe(OH)\(_3\), Fe\(_2\)O\(_4\),
Fe\(_2\)O\(_3\), FeOOH, Fe\(_5\)HO\(_8\)·4H\(_2\)O). The various forms of iron oxides, oxyhydroxides, and
hydroxides are called “iron oxides” through the end of this paper. Thus, in an aqueous
solution, Fe\(^0\) ideally converts to crystalline iron oxides via a sequence of oxidation/
hydrolysis/precipitation/dehydration reactions (Tab. 1). The conversion of Fe\(^0\) to crystalline
iron oxides goes towards several intermediate stages of amorphous and poorly crystalline
precipitates, including green rust formation and transformation. Intermediate stages also
include solid-state transformation of oxides (recrystallisation). For example, in aqueous
solution crystalline Fe(OH)\(_2\) may convert to other iron oxides via
oxidation/hydrolysis/dehydration.

In essence, iron oxide formation involves two basic mechanisms: (i) direct precipitation from
Fe\(^{2+}\)/Fe\(^{3+}\)-containing solutions, and (ii) transformation of an Fe oxide precursor. Both
mechanisms may occur in natural Fe\(^0\)/H\(_2\)O systems, even though direct precipitation is
dominant. Due to the diversity of iron corrosion products (CP), a common problem faced by
studies on Fe\(^0\)/H\(_2\)O systems is the proper characterization of available iron oxides (37-39). A
common procedure is the use of synthetic iron oxides to simulate natural CP. However, in
natural Fe\(^0\)/H\(_2\)O systems, CP are composed primarily of different iron oxides. Individual iron
oxides possess different chemical properties such as crystal structure, morphology, and
adsorptive properties (Tab. 2). Accordingly, no synthetic iron oxides (or oxide mixtures) can
rigorously simulate natural CP with regard to transformation occurring within.

**Transformations within Fe\(^0\)/H\(_2\)O systems**
Synthetic iron oxides as simulates for natural iron oxides are prepared in the pure phase while natural oxides are precipitated and further transformed in the presence of foreign species (including contaminants). Thus a synthetic oxide can remove contaminant solely by adsorption while natural oxides incorporate contaminant in their structure while precipitating (adsorption and co-precipitation). At any moment after implementation of a Fe\(^0\) reactive wall, a natural Fe\(^0\)/H\(_2\)O system is made up of Fe\(^0\) and various iron oxides, possibly including transforming phases like FeO which are not stable under natural (sub)surface conditions.

Given that the iron oxides are of various reactivity toward contaminant removal, the contribution of individual removal mechanisms to decontamination is difficult to access. However, it is the goal of this paper to demonstrate that, beside adsorption, contaminant sequestration (co-precipitation) is the sole certain removal mechanism. The occurrence and the extent of all other processes can be discussed on a contaminant-specific basis. Therefore adsorption and co-precipitation are the fundamental mechanisms of contaminant removal in Fe\(^0\)/H\(_2\)O system. To illustrate the transformations yielding to contaminant sequestration, the evolution of three iron atoms from the Fe\(^0\) material will be discussed.

The three atoms (3 Fe\(^0\)) will be first oxidized to 3 Fe\(^{II}\) species and may further be oxidized (e.g. by O\(_2\)) to 3 Fe\(^{III}\) species. Then they will be transformed to colloidal species partly having specific surface areas (SSA) higher than 500 m\(^2\)/g (43, 44) before they aggregate and crystallize to one Fe\(_3\)O\(_4\), 1.5 Fe\(_2\)O\(_3\) or 3 Fe(OH)\(_2\), Fe(OH)\(_3\) or FeOOH. The relative variation of the volume of resulted crystalline oxides is represented in Fig. 1 using values from Tab. 2. Fig. 1 clearly shows volume expansion relative to 3 Fe\(^0\) for all iron oxides except magnetite for which a volume reduction of 30 % was noticed. However, it should be kept in mind that even magnetite is a final state of a transformation going through even more voluminous colloidal, amorphous and highly adsorptive species (SSA values in Tab. 2). Although volume expansion is discussed here on the basis of the volume of crystallized iron oxides, this process is a rule in the process iron corrosion, irrespective from the nature and the crystallinity of the
final products. Thus iron oxidative dissolution and iron oxide precipitation should by regarded a cycle of volume expansion/contraction in the course of which available contaminants are adsorbed and sequestrated. Sequestrated contaminants could be further transformed (oxidized or reduced).

**Conclusions**

This paper has contributed to open a new avenue for the scientific understanding of processes of contaminant removal in Fe\(^0\)/H\(_2\)O systems. Researchers and practitioners have long recognized the limits of the reductive transformation concept (11-14). However, the view that contaminants are primarily adsorbed and co-precipitated with iron corrosion products (29, 30, 33) has partly faced with very sceptic views (45, 46) or is just degraded to an “alternative hypothesis to be considered” (47). Fortunately, sceptic views are based on the large acceptability of the concept of reductive transformation which was a consensus (4) and not of hard experimental facts. While former attempts to disprove the reductive transformation concept were based on extensive literature review (29, 30) and a munitions examination of the abundance of reactive species in Fe\(^0\)/H\(_2\)O systems (33), the present study is based on a simple analysis of processes occurring in a Fe\(^0\)/H\(_2\)O system. The major output is that Fe\(^0\) oxidative dissolution and iron oxide precipitation should by regarded as a cycle of volume expansion/contraction in the course of which chemical contaminants and pathogens are adsorbed and sequestrated. Because this argument does not care about the nature of a contaminant, it should be definitively clear that specific interactions are an exception and not the rule in a Fe\(^0\)/H\(_2\)O system (statement 1). Statement 1 is the cornerstone on which comprehensive knowledge on the behaviour of Fe\(^0\)/H\(_2\)O systems under natural conditions should be acquired. In this effort, it is almost impossible to transfer good results from the open aqueous iron corrosion. For example, corrosion inhibition of mild steel by methylene blue (MB) has been reported (48). However, corrosion inhibition is effective with 5.0 mM (1595 mg/L) MB in HCl at temperatures varying from 30 to 60 °C. The used temperatures are
not relevant for groundwater remediation and the needed concentration (1595 mg/L) is even
non relevant for wastewater situations. Additionally the reaction took place in a strong acidic
solution (2 M HCl).

Acknowledgments

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   51.


Table 1: Relevant reactions for the process of aqueous Fe<sup>0</sup> dissolution, iron corrosion products formation and contaminant (Ox) removal in Fe<sup>0</sup>/H<sub>2</sub>O system. Red is a reduced form of Ox. FeOOH is a proxy of corrosion products and Fe<sub>x</sub>(OH)<sub>y</sub>~(3x-y)~ is an iron hydroxide.

<table>
<thead>
<tr>
<th>Process</th>
<th>Reaction</th>
<th>Eq.</th>
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</thead>
<tbody>
<tr>
<td>Fe&lt;sup&gt;0&lt;/sup&gt; dissolution</td>
<td>Fe&lt;sup&gt;0&lt;/sup&gt; ⇄ Fe&lt;sup&gt;2+&lt;/sup&gt; + 2 e&lt;sup&gt;-&lt;/sup&gt;</td>
<td>1</td>
</tr>
<tr>
<td>Fe&lt;sup&gt;0&lt;/sup&gt; passivation</td>
<td>Fe&lt;sup&gt;0&lt;/sup&gt; + H&lt;sub&gt;2&lt;/sub&gt;O ⇌ Fe(O)&lt;sub&gt;ads&lt;/sub&gt; + 2 H&lt;sup&gt;+&lt;/sup&gt; + 2 e&lt;sup&gt;-&lt;/sup&gt;</td>
<td>2</td>
</tr>
<tr>
<td>Fe&lt;sup&gt;0&lt;/sup&gt; depassivation</td>
<td>Fe(O)&lt;sub&gt;ads&lt;/sub&gt; + 2H&lt;sup&gt;+&lt;/sup&gt; ⇌ Fe&lt;sup&gt;2+&lt;/sup&gt; + H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>Fe(O)&lt;sub&gt;ads&lt;/sub&gt; + H&lt;sub&gt;2&lt;/sub&gt;O ⇌ Fe(OH)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>Fe(O)&lt;sub&gt;ads&lt;/sub&gt; + OH&lt;sup&gt;-&lt;/sup&gt; ⇌ HFeO&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;-&lt;/sup&gt;</td>
<td>5</td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt; evolution</td>
<td>2 H&lt;sup&gt;+&lt;/sup&gt; + 2 e&lt;sup&gt;-&lt;/sup&gt; ⇌ H&lt;sub&gt;2&lt;/sub&gt;↑</td>
<td>6</td>
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<tr>
<td>O&lt;sub&gt;2&lt;/sub&gt; reduction</td>
<td>O&lt;sub&gt;2&lt;/sub&gt; + 2 H&lt;sub&gt;2&lt;/sub&gt;O + 4 e&lt;sup&gt;-&lt;/sup&gt; ⇌ 4 OH&lt;sup&gt;-&lt;/sup&gt;</td>
<td>7</td>
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<tr>
<td>Fe&lt;sup&gt;2+&lt;/sup&gt; oxidation</td>
<td>Fe&lt;sup&gt;2+&lt;/sup&gt; ⇌ Fe&lt;sup&gt;3+&lt;/sup&gt; + e&lt;sup&gt;-&lt;/sup&gt;</td>
<td>8</td>
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<tr>
<td></td>
<td>Fe&lt;sup&gt;2+&lt;/sup&gt; + 2 OH&lt;sup&gt;-&lt;/sup&gt; ⇌ Fe(OH)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>Fe&lt;sup&gt;3+&lt;/sup&gt; + 3 OH&lt;sup&gt;-&lt;/sup&gt; ⇌ Fe(OH)&lt;sub&gt;3&lt;/sub&gt;</td>
<td>10</td>
</tr>
<tr>
<td>Scale formation</td>
<td>Fe(OH)&lt;sub&gt;2&lt;/sub&gt; ⇌ FeO + H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>2 Fe(OH)&lt;sub&gt;3&lt;/sub&gt; ⇌ Fe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt; + 3 H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>4 Fe(OH)&lt;sub&gt;3&lt;/sub&gt; ⇌ Fe(OH)&lt;sub&gt;2&lt;/sub&gt; + Fe&lt;sub&gt;3&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt; + 5 H&lt;sub&gt;2&lt;/sub&gt;O + ½ O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>Fe(OH)&lt;sub&gt;3&lt;/sub&gt; ⇌ FeOOH + H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>14</td>
</tr>
<tr>
<td>O&lt;sub&gt;x&lt;/sub&gt; reduction</td>
<td>Fe&lt;sup&gt;0&lt;/sup&gt; + OX&lt;sub&gt;(aq)&lt;/sub&gt; ⇌ Fe&lt;sup&gt;2+&lt;/sup&gt; + Red (s or aq)</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>Fe&lt;sup&gt;II&lt;/sup&gt;&lt;sub&gt;(aq)&lt;/sub&gt; + OX&lt;sub&gt;(aq)&lt;/sub&gt; ⇌ Fe&lt;sup&gt;III&lt;/sup&gt; + Red (s or aq)</td>
<td>16</td>
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<tr>
<td></td>
<td>Fe&lt;sup&gt;II&lt;/sup&gt; (s) + OX&lt;sub&gt;(aq or aq)&lt;/sub&gt; ⇌ Fe&lt;sup&gt;III&lt;/sup&gt; + Red (s or aq)</td>
<td>17</td>
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<tr>
<td></td>
<td>H&lt;sub&gt;2&lt;/sub&gt; + OX&lt;sub&gt;(aq or aq)&lt;/sub&gt; ⇌ H&lt;sup&gt;+&lt;/sup&gt; + Red (s or aq)</td>
<td>18</td>
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<tr>
<td>O&lt;sub&gt;x&lt;/sub&gt; adsorption</td>
<td>FeOOH + OX&lt;sub&gt;(aq)&lt;/sub&gt; ⇌ FeOOH-Ox</td>
<td>19</td>
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<tr>
<td>O&lt;sub&gt;x&lt;/sub&gt; co-precipitation</td>
<td>OX&lt;sub&gt;(aq)&lt;/sub&gt; + n Fe&lt;sub&gt;x&lt;/sub&gt;(OH)&lt;sub&gt;y&lt;/sub&gt;<del>(3x-y)</del> ⇌ Ox[Fe&lt;sub&gt;x&lt;/sub&gt;(OH)&lt;sub&gt;y&lt;/sub&gt;<del>(3x-y)</del>]&lt;sub&gt;n&lt;/sub&gt;</td>
<td>20</td>
</tr>
</tbody>
</table>
Table 2: Some relevant characteristics of metallic iron and its main corrosion products. SSA is the specific surface area. $V_{\text{rust}}/V_{\text{Fe}}$ is theoretical ratio between the volume of expansive corrosion products and the volume of iron in the Fe$^0$ material. Data from refs. 40-42.

<table>
<thead>
<tr>
<th>Species</th>
<th>Formula</th>
<th>Symmetry</th>
<th>Density (m$^2$/g)</th>
<th>SSA</th>
<th>$V_{\text{rust}}/V_{\text{Fe}}$</th>
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<tr>
<td>Iron</td>
<td>Fe</td>
<td>bcc</td>
<td>7.86</td>
<td>&lt;1</td>
<td>-</td>
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<tr>
<td>Magnetite</td>
<td>Fe$_3$O$_4$</td>
<td>Cubic</td>
<td>5.18</td>
<td>6.0</td>
<td>2.08</td>
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<td>Hematite</td>
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<td>Rhombohedral</td>
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<td>64</td>
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<tr>
<td>Maghemite</td>
<td>$\gamma$-Fe$_2$O$_3$</td>
<td>Cubic</td>
<td>4.69</td>
<td>30</td>
<td>n.a.</td>
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<tr>
<td>Goethite</td>
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<td>4.28</td>
<td>82</td>
<td>2.91</td>
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<td>3.35</td>
<td>328</td>
<td>4.2</td>
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n.a. = not available.
Figure 1: Relative volumes of iron and selected crystalline corrosion reaction products. The values is the bar represent the expansion coefficient. The calculations were made for three iron atoms and show that a volume compression will occur upon formation of Fe$_3$O$_4$. Strictly any crystallization goes through dissolution, nucleation and aggregation. Intermediate species are of high specific area and even more voluminous than crystalline Fe(OH)$_3$. 