

Metallic iron for water treatment and environmental remediation: A handout to young researchers

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Abstract

The premise of this research note is that current research on metallic iron (Fe^0) for environmental remediation and water treatment has started on a biased basis. Before expecting experienced researchers to correct flawed approaches compromising the future of the technology, the attention of new researchers should be drawn on the prevailing flawed conceptual models. There are guides on how to select good research topics, to perform good literature review, to select good mentors, and to write good scientific papers. But critically reviewing the published material is part of the competence of any new researcher in a given field of research. This research note summarizes the most critical issues of research on Fe^0 for water treatment as asks some key questions which would help research beginners to find their way.

Key words: Environmental remediation, Literature review, Peer review system, Water treatment, Zero-valent iron.

1 Introduction

There is evidence that environmental sciences are not in a golden age. A severe imbalance exists between money available for research and the growing scientific community worldwide [1]. Such imbalance has created the need of prioritization of research issues. The prioritization has created, in turn, a high competitive atmosphere in which scientific productivity is reduced. The reasons are numerous of which three can be named: (i) it is not likely that the few research groups receiving funding will produce good results, (ii) the reasons to disregard a research issue might not be objective and (iii) there is diminished time for scientists to think and perform productive work. These facts make it easy to acknowledge that the current system contains systemic flaws that are threatening its future.

Research on metallic iron (Fe^0) for environmental remediation and water treatment has started some 25 years ago [2-9] and has attracted the attention of the global research community. The golden age of research on 'Fe⁰ for the remediation industry' (remediation Fe⁰) is probably over as always limited funding is available for related research [10]. There is a general dramatic decline in success rates for grant applicants both at national and international levels [1,10]. However, there is evidence that the whole research performed during the golden age of remediation Fe⁰ was probably biased by a wrong premise. Actually, this research is documented in some 2,466 scientific publications (SCOPUS search with "zero-valent iron" in "titles, abstracts and key words" on January 26th 2015). Meaning that a research beginner on remediation Fe⁰ should virtually read some hundreds of papers to have an overview on the state-of-the-art knowledge.

The objective of this research note is to assist any research beginner in evaluating the available literature and fine-tune the aspect he wants to investigate. The presentation will start with the main features of the Fe⁰/H₂O system, followed with the popular state-of-the-art knowledge within the remediation Fe⁰ community, then an alternative view will be given. The

presentation will end with tool facilitating the choice of the research beginner for the better concept.

2 The Fe⁰/H₂O system

When a reactive Fe⁰ particle is introduced in water, Fe⁰ undergoes oxidative dissolution and generated Fe^{II} species (Eq. 1, Tab. 1). At pH > 4.5, Fe^{II} species are hydrated and tend to polymerize and precipitate as hydroxides (Fe(OH)₂) and oxides (Fe₃O₄) on the metal surface (or at its vicinity). The low solubility of Fe^{II} species at neutral pH values drives precipitation [11]. When Fe^{II} is oxidized to Fe^{III} (Eq. 2), iron precipitation is even more favorable because Fe^{III} species are less soluble than Fe^{II} ones. In essence, aqueous iron corrosion is an electrochemical process. The two main features are the electrical conduction of the two phases: (i) electronic conduction in the non corroded metal (Fe⁰ - electrode) and ionic conduction in the aqueous phase (electrolyte). In the course of iron corrosion, charge transfer occurs at the metal/electrolyte interface.

Fe⁰ oxidation releases electrons (Eq. 1) which must be consumed to ensure electrical neutrality. Accordingly, at least one reduction reaction (cathodic reaction) of a relevant chemical species present in the aqueous phase must happens simultaneously at the Fe⁰/H₂O interface (mostly H₂O and O₂ – Eq. 3 and Eq. 4). In other words, relevant cathodic reactions involve species that are able to (quantitatively) reach the Fe⁰ surface. Because the Fe⁰ surface is permanently shielded with an oxide scale (a physical barrier), the most common cathodic reaction is the reduction of water (H₃O⁺ ions) (Eq. 3) [12]. Clearly, the frequently cited Eq. 4 is only indirectly favored as iron corrosion is accelerated when Fe²⁺ species (Eq. 1) are consumed (LeChatelier Principle) [13,14]. Further processes responsible for contaminant removal in Fe⁰/H₂O systems are described in Tab. 1.

The last important feature of the Fe⁰/H₂O system is related to the omnipresence of the oxide scale (Eq. 11) at the surface of Fe⁰. In essence, there is no Fe⁰/H₂O interface (inexistent in Pourbaix diagrams), but at least two interfaces: Fe⁰/Fe-oxides and Fe-oxides/H₂O. In other

words, the (quantitative) transfer of electrons from Fe^0 to dissolved species is only possible if the oxide scale is electronic conductive. Such conductive oxide scales have not been reported, even under anoxic conditions [15,16]. On the other hand, the primary iron corrosion products (Fe^{II} and H_2/H) are reducing agents which reductive capacity is increased by the catalytic effects of the surface of oxides (secondary corrosion products) [17]. Clearly, although Fe^0 corrosion under environmental conditions is an electrochemical reaction, the reduction of dissolved species (including O_2) is not (necessarily) the simultaneous cathodic reaction [18]. These dissolved species are likely transformed by a chemical reaction with primary corrosion products (Fe^{II} and H_2/H) and secondary and tertiary corrosion products like Fe_3O_4 or green rusts.

3 The prevailing view of the $\text{Fe}^0/\text{H}_2\text{O}$ system

The popular state-of-the-art knowledge can be read in several recent overview publications [9,19-22]. The research community on remediation Fe^0 widely randomly interchanges ‘*reduction in the presence of Fe^0* ’ and ‘*reduction by Fe^0* ’ [23]. As recalled in § 2, this is not acceptable as ‘*reduction by Fe^0* ’ supposes that reducing electrons come from the metal body (direct reduction, electrochemical reaction). On the contrary, ‘*reduction in the presence of Fe^0* ’ is correct because Fe^0 is the parent of Fe^{II} , H_2/H and all other abiotic reducing species present in the $\text{Fe}^0/\text{H}_2\text{O}$ system. Regarding Fe^0 as own reducing agent has mediated many discrepancies in the literature.

The most obvious discrepancy is perhaps that Fe^0 is a better environmental remediation agent than Al^0 and Zn^0 . The standard electrode potentials (E^0 values) for the systems are: $\text{Fe}^{\text{II}}/\text{Fe}^0$: -0.44 V, $\text{Zn}^{\text{II}}/\text{Zn}^0$: -0.76 V and $\text{Al}^{\text{III}}/\text{Al}^0$: -1.66 V, suggesting that Fe^0 is the least powerful reducing agent. If Fe^0 was an own reducing agent, this observation would have challenged founded knowledge from General and Analytical Chemistry using Zn^0 where Fe^0 has failed to yield satisfactorily reducing results (E^0 values). The reason for the better efficiency of Fe^0 has

been identified as the fact that no protective oxide scale is formed at the surface of Fe^0 unlike on the surface of Al^0 and Zn^0 [24].

Another sloppy argumentation concerns ways to improved Fe^0 efficiency. The presentation in § 2 suggests that improving Fe^0 corrosion can be achieved in two major ways: (i) increasing the electronic conductivity of the metal body (e.g. using bimetallic systems), (ii) increasing the ionic conduction in the aqueous phase (e.g. addition of NaCl). Actually, the Fe^0 literature is full of examples considering increased contaminant reduction by bimetallic systems, by nano-scale materials or in the presence of certain co-solutes as proofs for reduction by Fe^0 [19-22]. However, as presented above (§ 2), all these improvements occur in the presence of Fe^0 . This means that documented increased contaminant reduction are more probably mediated by iron corrosion products (indirect reduction).

Because designing a system in which contaminants are reduced by Fe^0 is necessarily different from designing a system in which contaminant are removed in the presence of Fe^0 , there may be flaws in the design of existing systems for remediation Fe^0 . The most obvious example is that hybrid systems (e.g. Fe^0 /pumice or Fe^0 /sand) have been reported more efficient than pure Fe^0 systems (100 % Fe^0) for the removal of several contaminants [25-28]. If Fe^0 was an own reducing agent and reductive transformation the removal mechanism, the rule of thumb will be valid “the more Fe^0 is present, the larger the extend of contaminant removal”.

4 The true nature of the $\text{Fe}^0/\text{H}_2\text{O}$ system

Some scientists promote dissemination of more accurate and detailed information on the “operating mode of $\text{Fe}^0/\text{H}_2\text{O}$ systems” to encourage the design of better and sustainable Fe^0 systems for water treatment and environmental remediation [29-37]. Preliminary results have provided much greater detail on the functioning of $\text{Fe}^0/\text{H}_2\text{O}$ systems [38-40] than commonly accepted models [9,19-22]. Moreover, the long lasting discrepancy about the suitability of admixing Fe^0 with inert aggregates has been determined [29,30].

Fe^0 research was erroneously introduced as a new field of research. However, important work on aqueous iron corrosion under environmental conditions had been going on for decades [15,16,41-47]. Moreover, fundamental knowledge on aqueous iron corrosion is available since the 1930s [23]. In particular, summarizing research efforts on the 1970s and 1980s, Stratmann and Müller [12] established that under atmospheric conditions, Fe^0 is oxidized by water (even present as moisture) (Eq. 3 - Tab. 1) and molecular oxygen is reduced by Fe^{II} (Eq. 5) (not by electrons from Fe^0 - Eq. 4). In other words, Stratmann and Müller [12] have clearly illustrated that the electrochemical nature of iron corrosion under environmental conditions does not imply that Fe^0 is the reducing agent for a molecule as small as O_2 . It is difficult under such circumstances to understand why huge molecules like azo dyes [48,49] would diffuse where O_2 has failed.

In 2009, Noubactep [31] published a short communication entitled “*An analysis of the evolution of reactive species in Fe^0/H_2O systems*”. This article demonstrated that there is a myriad in-situ generated species in any Fe^0/H_2O system which by their activities make the system a universal decontamination one. Removing mechanisms being adsorption, co-precipitation and (adsorptive) size-exclusion. It is important to insist that reduction is not a stand-alone removal mechanism, in particular in the context of safe drinking water provision. In fact, in the environmental remediation context, reducing a species to a more biodegradable one can be a true solution while in the drinking water context, even reduction products (metabolites) should be removed from the aqueous phase. This clarification definitively demonstrates that chemical reduction is not always the solution, whereas removal is the common goal.

5 Discussion

There is repeated evidence of selective (non) referencing of articles reporting on the research conducted on the “*true nature of the Fe^0/H_2O system*” (§ 4). Two examples for illustration: Giles et al. [50] have referenced six (6) papers co-authored by Noubactep in a review article

entitled *'Iron and aluminium based adsorption strategies for removing arsenic from water'*, thus only partly dealing with Fe^0 materials. In the second example Fu et al. [19], Vodyanitskii [20,21] and Colombo et al. [9] have not mentioned that the concepts they are reviewing have been challenged. These two examples may be regarded as a hint for general carelessness in applying basic standards of sound scientific procedures/standards. But this is also a chance for a research beginner to demonstrate his ability to perform a critical literature review.

The reductive transformation model for remediation Fe^0 has never been univocally established [51-54] and was severely questioned/refuted in the peer-reviewed literature in 2007 [29,30]. However, 7 years later, published articles are still favouring the questioned model [9,19-22,55]. These publications are partly co-authored by leading scientists and are screened by reviewers and editors of international journals. On the other hand, many of the papers have been examined by promotion committees of Master and PhD students. Lastly, some habilitation thesis have been focused on remediation Fe^0 [18,56,57]. In other words, a PhD candidate (as research beginner) could have to challenge the work that has made his supervisor, a professor.

The presentation herein suggests that there is currently a crisis of confidence within the remediation Fe^0 community about the reliability of research findings. Why does the reductive transformation model for the $\text{Fe}^0/\text{H}_2\text{O}$ system persist in the scientific literature? Is it a function of insufficient cross-disciplinary approaches? Is the limited understanding of the $\text{Fe}^0/\text{H}_2\text{O}$ systems sustained by commercial interests? What biases are embedded in the language used to describe the $\text{Fe}^0/\text{H}_2\text{O}$ system in journal articles and technical reports? There is nobody better than research beginners [49,58,59] in the remediation Fe^0 community to help resolving these questions and contribute to progress in knowledge.

6 Conclusion

The remediation Fe^0 research community cannot continue to ignore the warning signs of a technology under stress and at risk of decline despite promising success stories. Larger

budgets for remediation Fe^0 are desirable, defensible and possible. In particular because Fe^0 for decentralized safe drinking water provision has the potential to warrant universal access to drinking water. All is needed is a front against structural flaws and sloppy science: A front to correct identified vulnerabilities. The changes need to begin immediately and widespread engagement with these changes is necessary, beginning with research beginners, individual scientists, academic institutions, funding agencies, and all other entities involved in scientific research.

The immediate goal of this research note has been to stimulate debate of an issue that concern the future of the Fe^0 remediation technology. This task cannot be left to a small group of (senior) scientists like those presented in § 4 who have already considering the named problems. Research beginners are therefore encouraged to seriously question the prevailing models. It is hoped that with this approach, critical actions on several fronts would soon save the fascinating and promising technology of “*putting corrosion to use*” [60].

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Table 1: Some relevant reactions involved in contaminant removal in the system Fe⁰/H₂O. Ox is the oxidized contaminant and Red its corresponding non or less toxic/mobile reduced form. x is the number of electrons exchanged in the redox couple Ox/Red. It can be seen that Fe⁰ and its secondary (Fe²⁺, H/H₂) and ternary (FeOOH, Fe₃O₄, Fe₂O₃) reaction products are involved in the process of Ox removal.

Reaction equation	Eq.
$\text{Fe}^0_{(s)} \Leftrightarrow \text{Fe}^{2+}_{(aq)} + 2 e^-$	(1)
$\text{Fe}^{2+}_{(s \text{ or } aq)} \Leftrightarrow \text{Fe}^{3+}_{(s \text{ or } aq)} + e^-$	(2)
$\text{Fe}^0_{(s)} + 2 \text{H}_2\text{O} \Rightarrow \text{H}_2\uparrow + 2 \text{OH}^- + \text{Fe}^{2+}_{(aq)}$	(3)
$2 \text{Fe}^0_{(s)} + \text{O}_2 + 2 \text{H}_2\text{O} \Rightarrow 4 \text{OH}^- + 2 \text{Fe}^{2+}_{(aq)}$	(4)
$4 \text{Fe}^{2+} + \text{O}_2 + 4 \text{H}^+ \Leftrightarrow 4 \text{Fe}^{3+} + 2 \text{H}_2\text{O}$	(5)
$x \text{Fe}^0 + \text{Ox}_{(aq)} \Rightarrow \text{Red}_{(s \text{ or } aq)} + x \text{Fe}^{2+}_{(aq)}$	(6) *
$2 \text{Fe}^0_{(s)} + 2 \text{H}_2\text{O} + \frac{1}{2} \text{O}_2 \Rightarrow 2 \text{FeOOH}$	(7)
$x \text{H}_2 + 2 \text{Ox}_{(aq)} \Rightarrow 2 \text{Red}_{(s \text{ or } aq)} + 2.x \text{H}^+$	(8)
$x \text{Fe}^{2+}_{(s \text{ or } aq)} + \text{Ox}_{(aq)} + \Rightarrow \text{Red}_{(s \text{ or } aq)} + x \text{Fe}^{3+}$	(9)
$2 \text{Fe}^{2+} + \frac{1}{2} \text{O}_2 + 5 \text{H}_2\text{O} \Rightarrow 2 \text{Fe}(\text{OH})_3 + 4 \text{H}^+$	(10)
$\text{Fe}(\text{OH})_3 \Rightarrow \alpha\text{-, } \beta\text{-FeOOH, Fe}_3\text{O}_4, \text{Fe}_2\text{O}_3$	(11) *
$\text{Fe}_2\text{O}_3 + 6 \text{H}^+ + 2 e^- \Rightarrow 2 \text{Fe}^{2+} + 3 \text{H}_2\text{O}$	(12)
$\text{Fe}_2\text{O}_3 + 2 \text{H}^+ + 2 e^- \Rightarrow 2 \text{Fe}_3\text{O}_4 + \text{H}_2\text{O}$	(13)
$8 \text{FeOOH} + \text{Fe}^{2+} + 2 e^- \Rightarrow 3 \text{Fe}_3\text{O}_4 + 4 \text{H}_2\text{O}$	(14)

* non stoichiometric