Water remediation by metallic iron: Much ado about nothing –
As profitless as water in a sieve?

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There has been much ado about water treatment with metallic iron (Fe\(^0\)) since the early 1990s. Thousands of articles, books, papers and technical reports have been written (i) describing laboratory feasibility tests, pilot plant performances and field implementations from around the world, (ii) outlining fundamental causes of failure (if applicable), and (iii) suggesting changes for more efficient Fe\(^0\) systems [1,2]. However, crucial knowledge about the operating mode of Fe\(^0\)-based systems is still lacking. In other words, fundamental knowledge necessary for the proper design of more efficient Fe\(^0\) remediation systems is still largely ignored [3]. To fill this knowledge gap and exploit the huge potential of Fe\(^0\) for water treatment, it is urgent to use a scientifically-based, truly interdisciplinary approach. Such a comprehensive, holistic and inclusive approach will unify a sound community in the quest of more efficient Fe\(^0\) remediation systems. This argumentation is not new as the funding policy of several agencies is based on ‘interdisciplinary approach’. In other words, an interdisciplinary approach is already largely followed. Yet still severe crises are encountered, in particular concerning the mechanism of contaminant removal in Fe\(^0\)/H\(_2\)O systems or even, concerning the intrinsic nature of Fe\(^0\). Is Fe\(^0\) a stand-alone reducing agent or a parent of (adsorbing, enmeshing and) reducing agents? The discussion on the nature of Fe\(^0\) is now lasting more than 6 years [4] but is still largely profitless. It seems, there is a lack of willingness to test new ideas even though the comfortable one is obviously not efficient.
The technology of treating water with Fe$^0$ was born with the spurious perception, that Fe$^0$ is a reducing agent [5]. This illusive view would have challenged almost a 200-years-old knowledge on the electrochemical nature of aqueous corrosion [6,7] and almost 100 years expertise from intensive research on aqueous iron corrosion [8]. In 1923, Ulick Richardson Evans (1889-1980) has provided a modern understanding of the corrosion process based on the electrochemical theory. Fortunately, the pioneers of the technology have not explicitly challenged the electrochemical theory of aqueous iron corrosion. They have simply ignored it and built a self-satisfactorily ‘knowledge system’ regarding Fe$^0$ as a reducing agent. This knowledge system can not explain why chemical species without any redox properties have been quantitatively removed in Fe$^0$/H$_2$O systems. Moreover, for Fe$^0$ to act as a reducing agent, electrons from the metal body should be relayed to the species of concern (including contaminants) by electronic conductive phases [5]. However, neither the multi-layer oxide scale on iron is conductive nor natural organic materials have been (univocally) positively tested as ‘electron shuttles’ [9-13]. In fact, the model of oxide scale generation and evolution sustaining the ‘reductive transformation’ concept [9] was proven inconsistent by Odziemkowski and colleagues [10-12]. Moreover, although magnetite films (Fe$_3$O$_4$) are electronic conductive in nature, the whole oxide scale on Fe$^0$ is always made of several layers including layers of Fe$^{III}$-species [14-16]. This evidence makes quantitative electron transfer from the metal body to species adsorbed at the outer surface of the oxide scale unlikely. In other words, all ‘crutches’ that have supported the introduction of the illusive concept have been proven false, but the concept is still miraculously alive.

A cursory look at the literature on remediation with Fe$^0$ reveals a vast scholarship originating from diverse disciplines and using Fe$^0$ of various types and sizes for multiple goals (e.g. environmental remediation, drinking water production, soil cleaning, wastewater treatment) [17-19]. The acronym “zero-valent iron” is used to designate elemental/metallic iron. That is iron in the oxidation state zero (Fe$^0$). The term ‘valence’ in “zero-valent iron” is wrongly
used. This misleading acronym is anterior to the Fe$^0$ remediation technology. However, Fe$^0$ is (still almost) univocally used as electron source for contaminant reductive transformation. Current and past researches aim to improve the understanding of interactions within the Fe$^0$/H$_2$O system, such that more efficient systems could be designed. It is obvious that no real improvement is possible when the intrinsic nature of Fe$^0$ is not established/recognized [20].

The intrinsic nature of aqueous metal corrosion is summarized in a paper by Sato [21] in the following terms: “Metallic corrosion produces a layer of corrosion precipitates on the metal surface in aqueous solutions. The interfacial layer thus produced influences the corrosion of underlying metals depending on its ionic and electronic properties. The presence of a gel-like or porous precipitate layer of insoluble rusts such as hydrous metal salts or oxides causes either accelerated metallic corrosion or passivation”. This text recalls that iron is corroded by water and that the Fe$^0$ surface is covered by oxide layers. These layers are non conductive as a rule. Accordingly, regardless from the background of any active researcher, his primary work should consist on elucidating how such a system will behave in the presence of target species, including the contaminants. If such an approach was adopted, a false concept would have not been introduced in the 1990s. Moreover, an alternative view would have not remain 7 years mostly untested.

Arguments against the alternative view are numerous and include the following: (i) the prevailing concept is well accepted, (ii) it is not worth to look nearly into the matter, (iii) the author has not presented experimental results, (iv) the author has already published this argument in other forums, (v) no better support of old arguments are given, and (vi) related articles appeared in ‘low impact journal’. Taken together this argumentation is not based on scientific facts and has even not really addressed the crucial point: the reductive transformation concept is simply false. The best pseudo-scientific argument will not correct this mistake. A more scientific attitude recommends that the inherently wrong concept is
abandoned and the alternative, already positively tested by few researchers [20,22-24] is considered as the new compass in exploring the \( \text{Fe}^0/\text{H}_2\text{O} \) universe.

There is indeed much ado about the operating mode of \( \text{Fe}^0/\text{H}_2\text{O} \) systems, as there should be. The critical issue of this discussion is the mechanism of contaminant removal. This issue is elegantly solved by simply properly considering the iron corrosion literature [14-16]. Alternatively, the thermodynamics of iron oxidative dissolution and the subsequent precipitation of iron phases can be considered. Instead of arguing with examples, scientists should have trusted the expertise of their colleagues who are closer in their academic background to electrochemistry [25,26]. Thus, it is argued that the operating mode of \( \text{Fe}^0/\text{H}_2\text{O} \) systems must be addressed comprehensively through sound interdisciplinary studies. In this effort, expertise of individual scientists should be respected. If individual expertise is not respected, the vast array of ‘scientific’ studies may just seep though the sieve of intellectual selfishness. This intellectual selfishness is as profitless as water in a sieve [27,28].

To conclude, the German thinker, Johann Wolfgang von Goethe (28.08.1749 - 22.03.1832) will be quoted: “In the sciences, people quickly come to regard as their own personal property that which they have learned and had passed on to them at the universities and academies. If someone else comes along with new ideas that contradict the Credo and in fact even threaten to overturn it, then all passions are raised against this threat and no method is left untried to suppress it. People resist it in every way possible: pretending not to have heard about it; speaking disparagingly of it, as if it were not even worth the effort of looking into the matter. And so a new truth can have a long wait before finally being accepted.” It is amazing, perhaps also surprising, to realize that this observation is valid even for an evidence resulting from a falsification of the mainstream corrosion science. It seems that the primordial motivation for scientific publication is no more the scientific content but some common ‘urgencies’ ("publish or perish"). Relevant ‘urgencies’ include patents, promotions, proposal success or salary increments [29]. "Publish or perish" is an excellent threatening reminder of
the importance of the publication of scientific achievements. However, despite simplified accessibility to scientific articles (e.g. SciFinder®, Scopus®, Web of Sciences®) dealing with Fe⁰, individual articles must be critically and impartially evaluated. In other words, the “So what?” question [30] should always be in the mind of each author, if scientific progress is sought.

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