

Opinion

Iron Corrosion: Scientific Heritage in Jeopardy

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Abstract: Research on the use of metallic iron (Fe^0) for environmental remediation and water treatment has taken off during the past three decades. The results achieved have established filtration on Fe^0 packed beds as an efficient technology for water remediation at several scales. However, the further development of Fe^0 -based filtration systems is impaired by the non-professional behavior of scientists who ignore available advances in knowledge. The confusion is overcome when due consideration is given to the fact that revealing state-of-the-art knowledge is a prerequisite to presenting individual achievements.

Keywords: academic writing; environmental remediation; iron corrosion; water treatment; zero-valent iron

The use of metallic iron (Fe^0) in the remediation of contaminated water is based on Fe^0 oxidative dissolution (aqueous iron corrosion) [1,2]. Iron corrosion produces various solid corrosion products (FeCPs—iron oxides and hydroxides) which interact with dissolved (i) contaminants, and (ii) further corrosion products (Fe^{II} , Fe^{III} and H/H_2). In other words, the $\text{Fe}^0/\text{H}_2\text{O}$ system is a dynamic system which is the home state of various species exhibiting adsorbing, oxidizing, precipitating and reducing properties [3–6]. It is therefore comprehensible that Fe^0 is used in situations in which contaminants are to be removed (adsorption and co-precipitation) or transformed (oxidation and reduction) [7–11]. Contaminants of concern are both biological and chemical in nature, making Fe^0 systems a potential support in the battle for a universally clean environment and safe drinking water, as defined by the UN Sustainable Development Goals (UN SDGs) [12].

In the early 1990s, Khudenko [13] demonstrated Fe^0 is an efficient material for inducing redox transformations (oxidation and reduction) of organic species. These redox transformations were coupled with the parallel oxidation of Fe^0 by salts of more noble metals (e.g. Cu^{2+} , Pb^{2+}) (cementation). At the same time, Fe^0 was introduced as a reducing agent for the reductive transformation of organic species after an electro-chemical mechanism (simultaneous reactions) [7,8,10,11,14]. Since then, Fe^0 has been presented in scientific literature as a reducing agent under environmental conditions [14,15]. The authors regard this situation as a danger for the integrity of science [16–18]: Fe^0 oxidative dissolution and contaminant reduction are not simultaneous (direct reduction) but parallel reactions (indirect reduction). On 27 October 2018, a Google search revealed that Khudenko [13] had been cited 13 times, while a Scopus search reveals only eight citations. These data suggest that Khudenko [13], which could have been the scientific foundation of Fe^0 -based technology, has been largely ignored by the majority of active researchers (including the authors).

A clear confusion was introduced in scientific literature as observed reductive transformations of dissolved species in the presence of Fe^0 were regarded as a cathodic reaction coupled to iron oxidative dissolution (anodic reaction—simultaneous reaction / direct reduction) [16–18]. For such a mechanism to be relevant, the universal oxide scale (FeCPs) shielding the Fe^0 surface (at pH values larger than 4.5)

needs to be electronically conductive. Such a conductive oxide scale has never been established under environmental conditions [19,20]. On the contrary, the oxide scale certainly acts as a diffusion barrier to dissolved species, including molecular oxygen (O₂). The oxide scale collects dissolved species which can then be reduced by Fe^{II} species and H₂ (Equation (1)). It is thus not surprising that species are reduced in Fe⁰/H₂O systems [3–6,21]. This is a pure chemical reaction between contaminants and primary iron corrosion products (Fe^{II}, H₂). Considering Fe⁰ as an own reducing agent is a mistake that is impairing progress in this promising branch of environmental engineering.



Scientific literature includes many articles that selectively present Fe⁰ as: (i) a reducing agent, (ii) a generator of HO· radicals; (iii) a generator of hydroxides and oxides (FeCPs); (iv) a generator of H₂ for biological processes; and/or (v) acting as catalysator to favor some chemical transformations [7,8,10,11,22,23]. While Fe⁰ alone or in combination with selected additives can achieve the assigned goals, the real operating mode was described in the peer-reviewed literature as early as 2007 (a full decade ago already) and has been largely ignored by the active Fe⁰ research community [3]. For example, it is difficult to provide convincing evidence that both oxidative and reductive processes occur in a Fe⁰/H₂O system, if their special areas of action are not properly considered. For example, electrochemical iron corrosion after Equation (1) always occurs both under anoxic and oxic conditions. Under oxic conditions, O₂ and other oxidizing agents are reduced within the oxide scale, possibly in the vicinity of the Fe⁰ surface but never at the shielded surface. Accordingly, iron corrosion is accelerated because Fe²⁺ is consumed (LeChatelier principle). Similarly, HO· radicals are not generated at the Fe⁰ surface. Despite this evidence, even recent articles describe Fe⁰/H₂O systems while confusingly referencing other challenging articles in the same batch.

The real operating mode of Fe⁰/H₂O systems is essential to promote the named technology by designing affordable, efficient and sustainable remediation systems, in particular for decentralized water supplies in low-income communities. This objective will not be achieved until the initial mistake has been acknowledged and corrected. It suffices to properly consider the work of Khudenko [13], a science-based concept that has been independently demonstrated by some researchers [3,21,24,25]. Admittedly, some efficient Fe⁰-based remediation systems exist, some even before the 1990s, but they were almost all designed using a pragmatic approach. For example, several household and small community filtration systems were developed using iron nails as reactive materials for arsenic removal [26,27]. However: (i) such filters are not specific for As; and (ii) commercial iron nails differ in their intrinsic reactivity. Differences in intrinsic reactivity may explain some cases of failure [28–30]. On the other hand, taking intrinsic reactivity as a key design parameter (material selection) will accelerate progress in designing efficient Fe⁰-based systems [31,32].

The production of research articles is comprehensively described as the way to ‘make the best better’ by improving the state-of-the-art knowledge. This implies that the available knowledge is reviewed and knowledge gaps, to be filled by the results set out, are clearly presented. It is surprising to learn that the century-old knowledge [1] that Fe⁰ is a generator of contaminant collectors for water treatment was overlooked during the 1990s. It is even more surprising that active researchers have not been properly considering: (i) the work of Khudenko [13] published in English in an accessible environmental journal (*Water Science and Technology*); and (ii) the decade-old corrections [3]. The question is: Can improvements be made when available knowledge is not fully considered? The absurdity of this situation becomes fully apparent when noting that articles that challenge the prevailing paradigm have been published in readily accessible journals over the years (e.g. *Environmental Science and Technology*, *Environmental Technology*, *Journal of Hazardous Materials*, *Water Research*) [3–6], including open access ones (e.g. *Open Environmental Science*, *Sustainability*, *Water*) [3,31,32].

The dynamic nature of iron corrosion (‘rust never rests’) still needs to be properly considered within the Fe⁰ research community as a whole [31,33]. The conventional approach to characterizing

available corrosion products at selected times merely provides an image of the system at these instants, in essence a static snap-shot. For example, if t_0 is the time of Fe^0 immersion and t_∞ is the time corresponding to Fe^0 complete exhaustion, the nature and the amount of available solid corrosion products (FeCPs) at any other time (t) depend on a myriad of inter-dependent factors. Relevant factors include: (i) the dissolved O_2 level; (ii) Fe^0 intrinsic reactivity; (iii) the Fe^0 proportion in the reactive zone; (iv) the Fe^0 size; (v) the nature and extent of water contamination; (vi) the nature and porosity of both Fe^0 and the aggregates used; (vii) the thickness of the reactive zone; (viii) the water chemistry (including the pH value); and (ix) the water flow velocity. To provide a complete picture, the biological and catalytic processes influencing the availability of FeCPs should be considered as well [12,32]. The diversity of relevant operational factors impacting the efficiency of $\text{Fe}^0/\text{H}_2\text{O}$ systems and the lack of unified operational testing procedures rationalize the abundance of discrepant reports while calling for science-based systematic investigations [12]. The design of such systematic studies should be grounded on state-of-the-art knowledge if progress in knowledge is the common goal. However, that seems to not be the case.

The Fe^0 -based remediation community is at war with itself; this is a premise for decline and the sole reason for this correspondence. The authors regard a communication without references to questionable research articles as a means to present an alarming situation to the whole scientific community without blaming individual researchers (or research groups). The appended references are merely a selection of review articles relating to the state-of-the-art knowledge. It is hoped that alerting the whole scientific community to misbehaviors within the environmental research community will contribute to their eradication. Most importantly, this communication presents the current situation to early-stage researchers (including PhD students) on 'Fe⁰ for water remediation', giving them a unique opportunity to start out on a better basis and make a better contribution to the achievement of the UN SDGs.

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