

Rescuing Fe⁰ remediation research from its systemic flaws

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Abstract

The well-accepted assumption of metallic iron (Fe⁰) acting as electron donor for environmental remediation has created an unstable domain of knowledge for the past 23 years. This assumption is discouraging some outstanding and prospective scientists from correctly interpreting their experimental results. Such a situation is a recipe for long-term decline. The critical situation cannot be solved with simplistic approaches. It is now imperative to develop an understanding to defend the difficulties of this assumption and re-orient Fe⁰ mediated remediation research as a whole.

Introduction

The research on using metallic iron (Fe⁰) for environmental remediation and water treatment is no more in a golden age. This opportunity can be used to address systemic flaws that have certainly threatened its development, and that were difficult to address some 10 years ago [1-3]. A central flaw is the long-held assumption that Fe⁰ is a direct reducing agent for the chemical transformation of contaminants [4-9]. As a result, the large majority of published works is still considering Fe⁰ as an environmental reducing agent [7,8,10-12]. The demonstration that this assumption has been a popular fallacy is now ten years old [2]. In a hyper-competitive atmosphere for research funding, scientific progress is broken as some have received their grants funded possibly for the propagation of misconceptions. Others have seen their grants rejected because they are dancing outside the circle. Thus, promising scientific careers are continued to be misdirected.

In retrospect, Fe⁰ remediation research was born with a mistake as the reductive transformation paradigm has never been convincingly established [13-16], but the flaw has been 'difficult' to recognize in the midst of success stories [17-24]. During the past two decades, Fe⁰ remediation researchers have (re) demonstrated the potential of Fe⁰ and Fe⁰-based filtration to remediate many cases of pollution including wastewater [10-12] and safe drinking water [25-30]. More than a century, Fe⁰ materials have been used in household water filters [31,32] and at large scale for the provision of cities [33-35]. More than 200 Fe⁰-based reactive walls are installed worldwide and are performing well [10,36]. Some rules of thumb are now available to design efficient and sustainable Fe⁰ filters, based on these and other achievements [37,38].

Despite such progress, it is remarkable that no bright future is generally expected from Fe⁰ filters [39-42]. Some systems have been almost abandoned [25,43] while even the proven efficient SONO filters [26,28] have not yet reached the expected large-scale distribution. The balance between 'expectations and achievements' are left out from the pure scientific perspective [44,45]. As an example, the very first Fe⁰ wall containing only 22% Fe⁰ (w/w) [14] is commonly referenced as a success story [10,16]. However, the majority of available Fe⁰ walls contain larger Fe⁰ proportions [21,22,24]. The rationale for their reported sustainability does not seem to have been discussed yet. Based

on these observations and evidences that alternative views have been constantly refuted [8,46-50] or belittled [51,52]. It is fair to argue that the Fe⁰ remediation research has progressed on an unsustainable path [53]. In the light of these findings, an attempt has been made in this communication to describe how this situation arose and proposes/reiterates some possible remedies. Critical analysis of the published literature revealed that the writing style has been given more attention and weightage than the scientific content.

Source of the misconception

The root cause of the widespread misconception is twofold: (i) the assumption that an observed chemical reduction of chlorinated solvents in a Fe⁰-based vessel is mediated by electrons from the metal body (reduction by Fe⁰, as a direct reduction) [54], and (ii) the consensus-based approach adopted in the initial stage of research on Fe⁰ for environmental remediation [14]. The research community must realize now that this misconception has created a non-precedent confusion [35,44,45,55-60]. Over the last decade, isolated researchers [8,23,61-68] have corrected the mistake but the large majority is still confounding 'reduction in the presence of Fe⁰ (including indirect reduction) and 'reduction by Fe⁰ (direct reduction-electrons from Fe⁰) [1-3,69,70].

The reductive transformation concepts

The idea that electrons from Fe⁰ mediate contaminant reductive transformations was adopted from a seminal work by Matheson and Tratnyek [4]. Although controversial views were published during 1994 and 1995 [13,71,72] Weber [6] validated and generalized the

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results of Matheson and Tratnyek [4]. Despite this pseudo-scientific demonstration supported by further reports [5,73,74], O'Hanessian and Gillham [75] acknowledged that the reductive transformation concept was a 'broad consensus'. Recently, Ebelle et al. [76] presented a detailed discussion of Matheson and Tratnyek [4]. It is clearly demonstrated that the conclusions of Matheson and Tratnyek [4] were not supported by own results. The question arises why could such a fallacy be introduced in the scientific literature? The evidence that the whole research community has ignored ancient works on using Fe⁰ for safe drinking water provision [31-35,77,78] is not addressed herein. Using metallic elements (including Al⁰, Fe⁰ and Zn⁰) for water treatment was also common place during the 1980s [79-83].

The propagation of the misconception

The Fe⁰ remediation technology was born in North America (Canada, USA) and 'migrated' to Australia, Europe and the rest of the world over the time [18,42,84-89]. The American colleagues were considered the absolute experts of the 'new born'. For example, the Fe⁰ remediation technology was introduced in Germany by a literature review [90] presenting the technology as an American innovation. The original literature review was improved two years later to account for novelties mostly based on not readily accessible technical documents [91]. The introduction of Fe⁰ walls in Italy and Belgium followed a similar path [42,84,85,87,89,92,93]. The mistakes transported in this trial have largely been identified and discussed [55,70,94-100] and will not be duplicated herein. It is sufficient to recall two aspects: (i) no initial critical review of the related scientific literature was performed and (ii) the iron mass balance was fully ignored. Interestingly, a vertical look through the list of authors reveals that many of them are members of editorial boards of authoritative journals. Authors and editors must endorse now the responsibility of the propagated misconception [101]. The next section illustrates the extent of confusion using the Fe⁰/Se system [102].

Lessons from the Fe⁰/Se system

The efficiency of Fe⁰ filings to remove Se from agricultural drainage water was demonstrated during the 1980s [80,82,103]. The operating mode of Fe⁰ filters for Se removal was elucidated by Anderson [82]. Accordingly, Fe⁰ serves as generator of contaminant collectors and Se^{VI}, Se^{IV} and Se⁰ are all adsorbed and/or occluded (co-precipitation) in the matrix of iron corrosion products (FeCPs). Fe⁰ filters were efficient but not sustainable because iron particles were soon cemented to each other and the initial porosity of the filters was filled by in-situ generated FeCPs (yielding permeability loss). In other words, Harza Fe⁰ filters were efficient but not sustainable.

With the advent of Fe⁰ reactive walls (permeable reactive barriers), the Fe⁰/Se system was 'rediscovered' and (mostly independently) intensively investigated over the past 17 years [15,40,102,103,104-113]. Se^{VI} was tested as redox-sensitive species to be reductively precipitated by Fe⁰. This effort was supported by an impressive number of modern analytical tools, using both bulk and surface methods [15,109,110,114,115]. Related studies tested several types of Fe⁰ materials including: (i) iron filings (IF), (ii) sponge iron and (iii) steel wool (SW). Available results can be summarized as follows: (i) Fe⁰ reduction can significantly decrease selenium concentrations at laboratory scale, (ii) Fe⁰ filters have successfully treated Se in full-scale operations at some sites, (iii) At some sites neither IF (granular Fe⁰) nor SW (fibrous Fe⁰) was efficient to meet regulatory requirements, (iv) at other sites SW were successful where IF failed and (v) no clear trend between the residence time in the filters and the efficiency could be established.

The example of the Fe⁰/Se system illustrates the extent of confusion within the Fe⁰ research community, despite available powerful analytical tools [38,53]. This communication advocates that the confusion is primarily due to the false assumption that Fe⁰ is a reducing agent. It appears that considering Fe⁰ as generator of Se collectors solves reported discrepancies and enable the design of (efficient and) sustainable filters. In fact, what is the long-term kinetics of Fe⁰ corrosion? Which Fe⁰ materials have the (long-term) ability to produce enough FeCPs for the collection of Se from the polluted water of concern? Answering these questions starts with two points: (i) avoiding pure Fe⁰ systems (columns with a zone containing 100 % Fe⁰) like in the Harza Process and (ii) characterizing the intrinsic reactivity of individual materials [38]. If such a systematic approach is broadly adopted, the modified Harza Process will be sustainable. Moreover, because co-precipitation and size-exclusion are primarily non (or less) selective mechanisms, Fe⁰ filters do not only address species with high affinities to FeCPS [59]. This is the rationale for making Fe⁰ filters as universal devices for safe drinking water and sanitation [38,69].

The assessment of the peer review system questioned

As it is now established that systematic flaws were governing research on Fe⁰ for environmental remediation [35,44,45, 53,55,57-61], there have been some injustice within the research community. In particular, the demands for research money is much larger than the supply. This hyper-competition is supposed to retain just the best scientific workforce for the limited funds available. However, in a context where the expertise of the referees is questioned, it appears that the best scientific workforce is rather punished for its clairvoyance. The great majority of environmental research is conducted by PhD students and postdoctoral fellows. But as a rule, the grants are obtained by more experienced scientists, including professors. In another phrase for two decades (5 generations of PhD student or 10 generations of postdoctoral fellows), experienced scientists working on Fe⁰ for environmental remediation have been the 'blind guide of the blind'. Consequently, a growing number of PhDs is graduating within a knowledge system inhibiting their creativity. In this vicious circle, they are performing a contra-productive job without advantage for the taxpayers' investment in their lengthy career of education. The current knowledge system on Fe⁰ remediation is a perpetual danger for the integrity of science.

Undermining the scientific knowledge-building process

Science is a collective activity aiming at building a reliable body of knowledge about the physical world. This goal can only be achieved if all scientists are honest and dedicated to the service of their respective nations. In this common project, there is no place for consensus and frauds. Admittedly, some consensus could be temporally met but just in the sake of more clarity. In other words, scientists who are committed to the task must take serious conscious steps to ensure that no falsehoods are introduced in the common knowledge database.

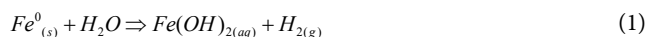
It is difficult to understand why scientists are undermining their own art. Hundreds of articles contain expressions like 'to the best of the author's knowledge' in the introduction to rationalize the investigation of things that are known for more than one century [33-35,77,78]. Moreover, several authors have put various arguments forward to maintain that Fe⁰ is an environmental reducing agent despite controversial views [8,46-52]. This attitude runs the risk of derailing the project of establishing the science of Fe⁰ remediation. Scientific knowledge-building should remain the paramount goal, whether it is accompanied by scientific scorekeeping or not.

Missing basic scientific rules

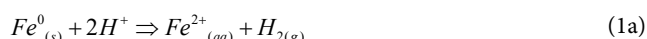
This section analytically describes the Fe⁰/H₂O system while ignoring primarily, intentionally achievements in the framework of 'Fe⁰ remediation'. The reader is then confronted with the dilemma of the 'Fe⁰ remediation' research.

An analysis of the Fe⁰/H₂O system

A piece of reactive Fe⁰ immersed in an aqueous solution undergoes spontaneous oxidative dissolution (aqueous iron corrosion) according to Eq. 1 (69,70):



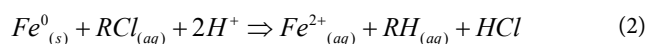
or



Equation 1 shows that Fe⁰ is a source of Fe^{II} and H species. Thus, Fe⁰ can be universally applied to generate Fe^{II} and H species (reducing agents) for any relevant application, including the generation of Fe^{III} and Fe^{IV} species [31,34,45,56,116]. Eq. 1 recalls that Fe⁰ is oxidized by water (H₂O) while Eq. 1a recalls that iron corrosion, and the corresponding H₂ generation, is more quantitative under acidic conditions (abundance of H⁺). Another explanation of Eq. 1a is that the consumption of H⁺ yields to an increase of the pH value.

Under anoxic conditions, Fe(OH)₂ is polymerized and precipitated as hydroxide which is mostly further transformed to magnetite (Fe₃O₄ or FeO.Fe₂O₃). A multi-layered oxide scale is formed on the Fe⁰ surface and acts as physical barrier for the transport of reactive species, from and to the Fe⁰ surface [1-3,117,119]. This is the rationale for the universally reported decreased kinetics of iron corrosion by the oxide scale [44,117,118]. It is essential to recall that under natural conditions (no external current), no direct Fe⁰ oxidation to Fe^{III} is possible. Moreover, Fe^{III} species are constantly present within anoxic Fe⁰/H₂O systems and their formation, rationalized by several mechanisms, is not addressed herein [119,120].

Under oxic conditions (presence of oxidizing agents including O₂), Eq. 1 is still the main reaction for aqueous iron corrosion [121]. Its reaction kinetics is accelerated by the consumption of Fe^{II} species (LeChatelier Principle) which are further oxidized to less soluble Fe^{III} species (mostly hydroxides and oxides). In another phrase, species reductive transformation in a Fe⁰/H₂O system results from a chemical reaction between Fe^{II} and H species (indirect reduction) and not from an electrochemical reaction (electrons from Fe⁰, direct reduction). Thus, reaction as per Eq. 2 is impossible under environmental conditions. RCl stands for a halogenated chlorinated hydrocarbon.



Three other important features of the Fe⁰/H₂O system are: (i) the volumetric expansive nature of iron corrosion [122], (ii) the fact that iron hydroxides precipitate in the presence of foreign species (co-precipitation) [123,124], and (iii) the evidence that iron hydroxides and oxides are good adsorbents for a wide range of dissolved species [29,125,126]. These three features act in synergy for the processes of aqueous contaminant removal in the presence of Fe⁰. In particular, in Fe⁰-based packed beds (Fe⁰ filters), volumetric expansion implies that porosity and thus permeability loss occurs with increasing operational duration. The progress of iron corrosion (corrosion rate) depends mainly on the porosity and stability of the oxide scale on Fe⁰ [117,118]. Thus, the importance of solution chemistry on the evolution of the oxide scale should be systematically characterized [38].

Separation processes in Fe⁰ Filters

Akageneite, amorphous iron hydroxides, goethite, green rusts, lepidocrocite, and magnetite are some common identified solid iron corrosion products from field and laboratory studies using Fe⁰ [21,22,127-131]. These minerals possess little or no permanent surface charge, but variable surface charge is generated through the adsorption of protons to surface hydroxyl groups [20]. For the near neutral pH range, it can be considered that iron oxides/hydroxides exhibit a positively charged surface [132]. This implies that Fe⁰ shielded with iron oxides cannot directly influence the transport of dissolved species to its surface. In other words, no matter the chemical reactivity of Fe⁰ towards a species (difference between the relative standard electrode potentials), the extent of its effective transformation depends on the species affinity to the oxide scale [59,132,133]: adsorption on the outer surface and diffusion through the film. This basic argument makes on the contaminant removal process makes unstable any discussion not properly considering the oxide scale as a physical barrier [1-3,35,44,45,55-60].

As an example, nitrate is considered a nonspecific ion that participate only in electrostatic ion exchange at the oxide surface, and do not undergo chemisorption through inner-sphere attachment [20,134]. This assumption is valid but must be completed by the size of NO₃⁻ and the diffusion potential across the oxide scale (porosity and tortuosity of the oxide scale). In other words, although the adsorption of some species (e.g. oxyanions) on iron oxides has been properly considered, diffusion behavior across the oxide scale has not been thoroughly examined. However, only such a holistic approach could enable the establishment of the science of Fe⁰ remediation.

Table 1 summarizes the key processes mediating contaminant removal in Fe⁰ filters. It is seen that a Fe⁰ filter acts as a media filter for the separation of particles, ideally only in-situ generated ones (iron oxides and hydroxides), but also as a chromatographic system for the separation of molecules. Iron oxides and hydroxides are generated in the presence of trace amounts of contaminants. Thus, contaminants are physically enmeshed in the matrix of these iron minerals (co-precipitation). Iron minerals can be regarded as contaminant collectors in Fe⁰ filters [31,32,135]. Lastly, because the precipitated iron minerals progressively fill the pore space within the filter, permeability loss occurs but contaminant removal by size-exclusion is increased [70,94-97].

Finally, two mechanisms should be shortly addressed here (precipitation and reduction) for an improved understanding. Both are quantitative at relatively high contaminant concentrations. Water treatment with Fe⁰ filters typically implies the removal of contamination at µg/L-level from large volume of waters. Under these conditions, neither precipitation nor reduction could be quantitative [136]. Moreover, the trace amounts of contaminants are immersed in an 'ocean' of iron hydroxides and oxides (oxide scale) such that the opportunity of a quantitative chemical reaction is not given [1-3].

Table 1. Separations processes involved in a Fe⁰-based filtration system.

Technique	Separated	Region A	Region B	Comments
Adsorption	Molecules	Filter	Filtrate	Highly selective
Co-precipitation	Molecules	Reactive zone	Filtrate	Non-specific
Precipitation	Ions	Filter	Filtrate	Not relevant
Reduction	Molecules/ions	Filter	Filtrate	Not relevant
Screening	Particles	On the screen	Past the screen	Increased efficiency
		Diameter > screen	Diameter < screen	with time
Size-exclusion	Molecules	Filter	Filtrate	Non-specific

For these reason chemical precipitation and reduction in the aqueous phase are not relevant in the context of environmental remediation and safe drinking water provision. In other words, the suitability of Fe⁰ for environmental remediation arises from its capacity to generate iron minerals which acts as contaminant collectors [26,82,69,135,136]. This knowledge was used by Tseng et al. [137] to concentrate ⁶⁰Co from sea water and by James et al. [138] to remove phosphate from wastewater. As discussed herein, contaminant reduction, when it occurs is mediated by iron corrosion products (e.g. Fe^{II}, H/H₂, green rusts, magnetite) and is not a relevant removal mechanism for any contaminant [70,95].

Back to the Fe⁰ remediation research

Fe⁰-based filters are an effective technology for environmental remediation [8,11,12,14,75,82,88], safe drinking water production [25-30,139], and waste water treatment (11,21-23,140). Fe⁰ barriers is an established technology for groundwater remediation [10,24]. Reported contaminant removal mechanisms include adsorption, biologically mediated transformations, chemical reduction (degradation/precipitation) and precipitation [20-24,35,56,57,58,67]. It is still mostly considered that Fe⁰ filters are to be used (i) for the dechlorination of halogenated hydrocarbons via reduction reactions, and (ii) for the reduction of heavy metals, relevant inorganic oxyanions (including nitrate and perchlorate) and radionuclides. Hereby, reduction is mostly regarded as a stand-alone removal mechanism and possible paths for contaminant reduction in Fe⁰/systems include: (i) direct reduction at the Fe⁰ surface, possibly via pitting in the oxide surface, (ii) reduction by dissolved Fe^{II} species, (iii) reduction by hydrogen species (H/H₂), and (iv) reduction by adsorbed Fe^{II} species (structural Fe^{II}) [21,141,142]. The removal of arsenic and selenium species have also been documented, but the importance of reduction was less emphasized [40, 108,134,143-147].

The analysis of the Fe⁰/H₂O system has demonstrated that this popular state-of-the-art knowledge on the operating mode of Fe⁰ filters is non-acceptable. In particular, because Eq. 1 is universal, all corrosion products are present in every Fe⁰/H₂O system. Accordingly, even where reduction is believed to play a key role, adsorbing agents are abundantly available [31,32,82,130,131,139] and have enmeshed some contaminant during their precipitation [1-3,56,59,61,62,67,70,95]. Moreover, screening (Table 1) is improved by porosity loss and contaminant removal by size-exclusion is not avoidable. Given that this knowledge is present in the peer-reviewed scientific literature since 2007 [2], it is difficult to understand why the reductive transformation concept is still prevailing [8]. Perhaps changes are more painful to some contemporary scientists than in the days of Carl Sagan. However, the objectivity is the main characteristic of science [148]. A view can be expressed aggressively, freshly, harshly or politely in one hand while it should remain objective on the other.

Should scientists learn from politicians?

In 1987, Carl Sagan stated: *"In science it often happens that scientists say, 'You know that's a good argument; my position is mistaken,' and then they would actually change their minds and you never hear that old view from them again. They really do it. It doesn't happen as often as it should, because scientists are human, and change is sometimes painful. But it happens every day"*. The continuation of the citation reads as: *"I cannot recall the last time something like that happened in politics or religion"*. Would researchers on Fe⁰ remediation agree with Carl Sagan?

It seems that nowadays, it is the scientist who must learn from politicians. In democratic systems, any politician confronted with any

single behaviour contrary to the constitution (the fundamental law of politics) should resign. Accordingly, any scientist confronted with a behaviour contrary to Chemical Thermodynamics (a fundamental law of chemistry) should rectify his understanding. If such an approach was universally adopted, the systematic flaw addressed herein would have not (i) been introduced and (ii) maintained for two decades. The situation is worsen by the evidence that the Fe⁰ filtration technology was introduced by distorting the stream of corrosion science and overseeing many other aspects of General Chemistry. In particular, the favoured reductive transformation concept is even not valid in the concentration range of concern (µg/L) [38,53,56,57]. Thus a paradigm shift of the current understanding for Fe⁰ filtration technology is very much demanding before the future researchers are dragged deeper into confusion [95].

Conclusions

The Fe⁰ remediation research community cannot continue to ignore the warning signs of a knowledge system under great stress. There is even a risk for incipient decline for an already proven efficient technology. It is certain that the tax payer will continue its strong support for a cleaner environment. It is also certain that desirable larger budgets for this aim are possible and defensible. However, for a purposeful use of such budgets, structural flaws within the system should be addressed in a systematic way. There is evidence that the established scientific approaches/methods can correct its vulnerabilities. Some fundamental changes are required to bring the Fe⁰ research community back on the highway of iron corrosion science. These changes need to be made in a comprehensive fashion. An immediate paradigm shift is called for considering the worsening of current situation during the last two decades. Widespread engagement is necessary to bring about this paradigm shift, beginning with immediate debate, strong advocacy for change, and action by individual scientists, the funding agencies, academic institutions, and other entities that control and pay for the conduct of science [149].

The envisioned future world of Fe⁰ researchers is not more or less talented than the current. It does not need more or less financial support as well. It will just perform better investigations based on the science of aqueous iron corrosion [117,118]. In this perspective, even small laboratories will restore an environment in which talented trainees and scientists can achieve excellent results within some years [38,59,150]. The immediate goal of this communication has been to stimulate the debate on important issues that concern the future of a potentially universal frugal technology, eventually based on a century old knowledge [31,32,33,34,35,77,78]. This task cannot be left to a self-appointed subset of scientists [56] or to the leaders of funding agencies. Therefore, academic institutions, scientific societies, funding organizations, and other interested parties are encouraged to organize discussions (at regional, national and international levels) with a wide range of relevant constituencies [149]. Some discussions of this type have already begun in countries like Cameroon, Germany, India, Lebanon, Romania and Tanzania [8,55,150-159]. However, critical actions are needed on several fronts by many parties to re-orient research on Fe⁰ for water treatment. No less than the future credibility of natural science is at stake.

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