

Investigating the processes of contaminant removal in Fe⁰/H₂O systems

Chicgoua Noubactep[†]

Angewandte Geologie, Universität Göttingen, Goldschmidtstraße 3, D - 37077 Göttingen, Germany,
Kultur und Nachhaltige Entwicklung CDD e.V., Postfach 1502, D - 37005 Göttingen, Germany
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Abstract—The instability of the premise of direct quantitative contaminant reduction by elemental iron (Fe⁰) materials in Fe⁰/H₂O systems is pointed out. Basic knowledge of aqueous iron corrosion shows that the Fe⁰ surface is not available for decontamination in nature. A comparison of the reactivity of Fe⁰ and Zn⁰ shows that the effectiveness of Fe⁰ materials for environmental remediation is due to the formation of a non-adhesive, porous oxide scale on Fe⁰. Contaminants are enmeshed within the scale and possibly reduced by Fe^{II} and H/H₂. An evaluation of current experimental conditions shows that well-mixed batch systems have disturbed the process of scale formation. Therefore, the majority of published works have operatively created conditions for contaminant reduction that are not likely to occur in nature. Since working under such unrealistic conditions has mediated the above-mentioned premise, interactions in Fe⁰/H₂O systems yielding contaminant removal should be revisited.

Key words: Adsorption, Decontamination, Reduction, Remediation, Zerovalent Iron

INTRODUCTION

The strong oxidation state dependent toxicity of several pollutants has prompted the development of remediation strategies that stimulate redox reactions in wastewaters, contaminated soils, sediments, and groundwater [1-13]. Thereby, hazardous species are transformed to less toxic or less mobile species through a redox reaction. For example, chromium(VI) reduction to chromium(III) substantially decreases this metal's solubility, mobility, and toxicity [12, 14]. The same principle governs the expected reduction of uranium(VI) to uranium(IV) [15-17]. Tested geochemical approaches include injection of reactive solutions [18,19], permeable reactive walls of elemental iron materials [4,20,21] or other reactive minerals such as FeS₂ and FeCO₃ [22-24], and injection of H₂S [25]. Bio-geochemical strategies rely on supplying organic carbon (OC) to stimulate direct microbial transformation of pollutants and indirectly microbially mediated reactions [26,27].

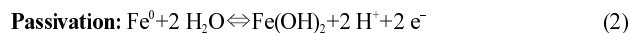
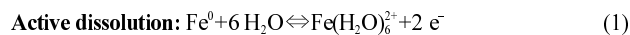
The use of Fe⁰-based alloys (zerovalent iron, Fe⁰ materials or Fe⁰) is based on the premise that quantitative contaminant removal in Fe⁰/H₂O systems is mostly due to contaminant reduction through electrons from the metal body (direct reduction) [28,29]. Because of the electrochemical nature of aqueous iron corrosion [30], this is only possible at the Fe⁰ surface or at the surface of an overlaying electrically conductive oxide-film (e.g., Fe₃O₄). However, given that under typical ranges of sub-surface pH (6 ≤ pH ≤ 9) there are several possible contaminant removal mechanisms (adsorption, co-precipitation, precipitation) in Fe⁰/H₂O systems, it is doubtful whether direct reduction may significantly contribute to contaminant removal as it is currently accepted, and repeated, in the introduction of many articles/books. For the sake of clarity, it should be stated that contaminant reduction is not a stand-alone removal mechanism as re-

duction products must be removed from the aqueous phase.

The objective of the present communication is to recall the instability of the concept of direct reductive contaminant removal through Fe⁰ in Fe⁰/H₂O systems, which is currently the main prop that holds up the iron reactive barrier technology. The study is based on a literature review of the process of iron corrosion and the reductive properties of Fe^{II} species and H/H₂. It is shown that quantitative contaminant removal can only occur within the film of corrosion products (oxide-film) at the vicinity of the Fe⁰ surface. The process of iron corrosion will first be presented, followed by a discussion of the contaminant interactions within the oxide-film and two strong arguments against direct reduction through Fe⁰ materials.

THE PROCESS OF AQUEOUS IRON CORROSION: OXIDE-FILM GENERATION

Under aqueous conditions elemental iron (Fe⁰) may dissolve (solvation) to an oxidized Fe^{II} specie (active dissolution or corrosion) according to Eq. (1), or form a second phase film - usually an insoluble 3D surface oxide-film (passivation) - according to Eq. (2):



Active dissolution and passivation are competing reactions. An oxide-film will form whenever the metal solubility is low (circumneutral pH values - Fig. 1). The further active metal dissolution (corrosion) depends on the protectiveness of the generated oxide-film. Whether a film is protective or not primarily depends on the relative unit-cells (packing distances or lattice parameters a, b, c, see Table 1) of the metal and its oxides [33,34]. In the case of iron, the unit-cells of the elemental metal and its oxides are not particularly close (Table 1); thus there is no tendency for an iron oxide-layer (oxide-film) to adhere to metallic iron (Fe⁰). An oxide-film instantaneously forms

[†]To whom correspondence should be addressed.
E-mail: cnoubac@gwdg.de

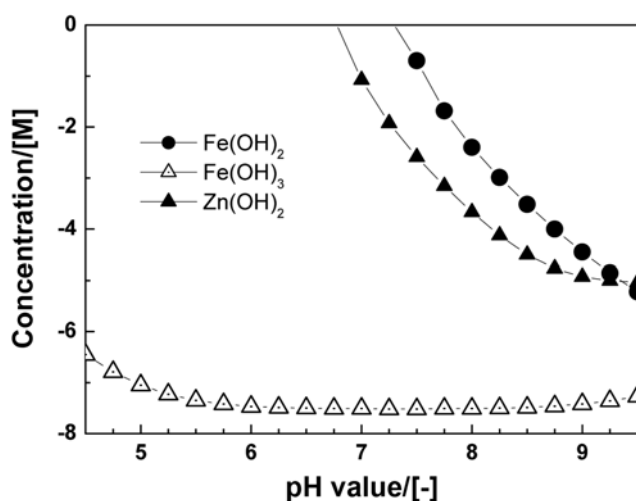


Fig. 1. pH dependence of metal hydroxide solubilities at pH values of natural waters. The trend for iron precipitation under oxic conditions (Fe^{III}) is clear and delineates the suitability of Fe^0 for water treatment by adsorption and co-precipitation. Even under anoxic condition $\text{Fe}(\text{OH})_2$ polymerize and readily precipitate. Data from ref. [32].

but is constantly flaked off and exposes fresh iron surface to the environment [33,34]. Iron corrosion will normally continue until the material is depleted.

The formation of an oxide-film on a Fe^0 -material upon aqueous corrosion is characteristic for $\text{pH} > 4.5$ [35,36] and further depends on several parameters: reactivity of the underlying Fe^0 -material, temperature, composition, and water flow velocity. These parameters determine the structure, the thickness and the porosity of the generated film. Such films grow by counter migration of Fe^{II} species from the Fe^0 surface (outward migration) and H^+ , O_2 , and other solutes from the flowing water (inward migration). Fe^{III} species are generated, they migrate, precipitate and are possibly reduced within the oxide-film. The driving forces for species transport are mostly electromigration (ionic species) and concentration gradients (all species).

The reaction scheme for film formation can be divided into four steps [37]: (i) active dissolution (Eq. (1)), (ii) transition range, (iii) pre-passive range, and (iv) oxide-film formation. In the transition and pre-passive range the metal becomes progressively covered by

$\text{Fe}(\text{OH})_2$ and/or $\text{Fe}(\text{OH})_3$ adsorbates. These adsorbates increasingly retard the active dissolution. The oxide-film is subsequently formed when the Fe^0 is completely covered with $\text{Fe}(\text{OH})_2/\text{Fe}(\text{OH})_3$ and deprotonization leads to the formation of a layer of iron oxide and oxyhydroxides (iron oxides: FeOOH , Fe_2O_3 , Fe_3O_4 , ...). It is very important to note that, once formed, the oxide-film should not be considered as a rigid layer, but instead as a system in dynamic equilibrium between film dissolution and film growth [37]. In other words, the oxide-film can adjust its composition and thickness to changing environmental factors (time, groundwater composition, temperature, microbial activity). In particular, the presence of some components (e.g. PO_4^{3-}) in groundwater may favor the production of insoluble corrosion products, possibly leading to an impervious and tenacious oxide-film. The corrosion reaction becomes self-limiting, as the corrosive medium can no longer diffuse through the oxide-film. Other groundwater components (e.g., Cl^-), will disturb the formation of continuous oxide-films or increase their porosity [38]. In this case Fe^0 active dissolution will continue until the material is depleted.

As already discussed, Fe^0 materials owe their suitability for groundwater remediation to the fact that the oxide-film continually flakes off and exposes the Fe^0 surface to the corrosive aqueous environment. However, new films are suddenly generated such that the bare Fe^0 surface is not accessible for contaminants as a rule. In fact, all contaminants (organic and inorganic) interact more or less strongly with the overlaying iron oxides [39]. The next section will discuss some of these interactions.

CONTAMINANT/OXIDE-FILM INTERACTIONS IN $\text{Fe}^0/\text{H}_2\text{O}$ SYSTEMS

As shown clearly, in a $\text{Fe}^0/\text{H}_2\text{O}$ system an interface $\text{Fe}^0/\text{H}_2\text{O}$ does not exist as a rule [17,35,40-42], but rather two interfaces: (i) Fe^0 /oxide-film, and (ii) oxide-film/ H_2O . Even though the metal surface may be temporally accessible at locations where the oxide-film is discontinued [40], this cannot be a rule. With these rare exceptions, to reach the Fe^0 surface, any contaminant must find its way across the oxide-film. Therefore, investigations regarding contaminant removal in $\text{Fe}^0/\text{H}_2\text{O}$ systems should always be conducted under conditions favoring the generation and the transformation of an oxide-film (ideally stagnant conditions, see below).

In a $\text{Fe}^0/\text{H}_2\text{O}$ system, a contaminant may be subject to four types

Table 1. Lattice parameters (a, b, c), structure and density of metallic iron and relevant corrosion products (iron oxides). The oxide-film on Fe^0 (rust) is an oxide mixture of different crystal structure than iron. Therefore the film is porous and poorly adherent (non-protective). Data from ref. [31]

Substance	Structure	Density (g/cm^3)	Lattice parameters (in Å)		
			a	b	c
Fe^0	Cubic	7.86	2.866	2.866	2.866
$\text{Fe}(\text{OH})_2$	Trigonal	3.40	3.27	3.27	4.62
FeOOH (gel)	Cubic		8.37	8.37	8.37
Fe_3O_4 (magnetite)	Cubic	5.175	8.396	8.396	8.396
FeOOH (goethite)	Orthorhombic	4.28	4.60	10.01	3.04
FeOOH (akageneite)	Tetragonal	3.55	10.52	10.52	3.028
FeOOH (lepidocrocite)	Orthorhombic	4.09	3.65	12.50	3.07
Fe_2O_3 (hematite)	Trigonal		5.035	13.72	5.26

of reactions: adsorption (physical and chemical), co-precipitation, oxidation and reduction. Oxidation reactions are not further considered in this communication. However, it is considered that oxidation products must be removed from the aqueous phase by adsorption, co-precipitation, precipitation or volatilization. Three different reduction pathways were specified [21,43,44]: (i) direct electron transfer from iron metal (direct reduction), (ii) catalyzed reduction by molecular H_2 (or atomic H) from H_2O reduction; the reaction is catalyzed by the Fe^0 surface or the Fe oxyhydroxides surface, (iii) catalyzed reduction by structural or dissolved Fe^{II} at the Fe oxyhydroxides surface (Fe^{II} derived both from iron corrosion and from oxide dissolution). Therefore, potential roles of the oxide-film include [41,45] (a) serving as an electron and ion transport barrier; hence reduction of solutes may occur primarily at pits or similar defects; (b) behaving as a conductor or semiconductor, which allows charge to pass across the interface with some resistance; (c) functioning as a catalyst, where adsorbed Fe^{II} (and H/H_2) provides strongly reducing surface sites, and (d) serving as Fe^{II} source whereas Fe^{III} oxides are reduced chemically (e.g., by H_2) or biologically.

The redox reactivity of a Fe^0/H_2O system is believed to primarily depend on the chemical thermodynamics of the two redox-systems of iron [46]: Fe^{II}/Fe^0 ($E^0 = -0.44$ V) and Fe^{III}/Fe^{II} ($E^0 = 0.77$ V). Therefore, the aim of using Fe^0 in groundwater remediation under anoxic conditions has been to exploit the negative potential of the couple Fe^{II}/Fe^0 to degrade or immobilize redox-labile contaminants (direct reduction). However, dissolved ferrous iron from the Fe^{III}/Fe^{II} redox couple can act as reductant for soil components (e.g., MnO_2) and contaminants (indirect reduction 1). Furthermore, it has been shown that adsorbed or structural Fe^{II} (structural Fe^{III}/Fe^{II} : $-0.34 \leq E^0(V) \leq 0.65$) can be more powerful in reducing contaminants [47] (indirect reduction 2) than the Fe^0 surface ($E^0 = -0.44$ V). On the other hand, recent results from Strathmann and co-workers [48] demonstrated that when complexed with organic substances, aqueous Fe^{II} (dissolved organic Fe^{III}/Fe^{II} : $0.520 \geq E^0(V) \geq -0.509$) is significantly more powerful than aqueous Fe^{II} ($E^0 = 0.77$ V) (indirect reduction 3). Therefore, abiotic contaminant reduction in a Fe^0/H_2O system does not necessarily take place by reduction through electron from Fe^0 (direct reduction). Keep in mind that this discussion considered molecular (H_2) and atomic (H) hydrogen as potential reducing agents without considering further details on the reaction mechanism.

Contaminant migration through an oxide-film to the Fe^0 surface may be a process which is limited by size exclusion effects [49]. Since contaminants are mostly larger than H_2O in their molecular sizes, in extreme cases inner layers of the film may only be accessible to protons (H^+) and water molecules (H_2O). Consequently, with decreasing porosity, iron is corroded merely by water (H_2O or H^+). Even under external (groundwater) oxic conditions oxygen may deplete completely within the oxide-film (e.g., through oxidation of Fe^{II} , as discussed above) [50]. In this case, contaminant reduction can only be the result of structural Fe^{II} or hydrogen (H or H_2) activity in the oxide-film or at the film surface. The reaction products remain adsorbed or are dissolved in groundwater depending on their relative affinity to iron oxides and groundwater chemistry.

Besides the molecular size of contaminants, their interactions with iron corrosion products (Fe^{II} -species, H/H_2) and the body of the transforming oxide-film are important. Since the oxide-film is a good adsorbent for both contaminants and Fe^{2+} ions (resulting in

more reactive structural Fe^{II}), contaminant reduction will certainly occur at the meeting point within the oxide-film, more or less far from the Fe^0 surface. In fact, Fe^{2+} ions from Fe^0 oxidation migrate in the direction of increasing pore sizes and contaminants in the opposite direction [51]. In all the cases quantitative contaminant reduction at the surface of Fe^0 is not likely to occur. Furthermore, irrespective of any interactions between contaminant and film materials (non-specific mechanism) [52], a contaminant can be entrapped in the matrix of precipitating and growing oxide-films (co-precipitation). A co-precipitated contaminant cannot further migrate to the Fe^0 surface. Such species will remain adsorbed and can be reduced by diffuse H/H_2 or Fe^{II} . Even physically adsorbed contaminants may be reduced within the oxide-film because of diffusion hindrances and the thermodynamic favorable catalytic reduction through H/H_2 or Fe^{II} . This affirmation is valid irrespective of the conductive properties of the oxide-film. Remember that direct reduction within or at the surface of the film is only possible if the oxide-film is electrically conductive. But even electrically conductive magnetite-layers, may passivate Fe^0 if they inhibit the migration of Fe^{2+} away from the surface.

This discussion reiterates that the formation of oxide-films at Fe^0 surfaces is an inherent process of aqueous iron corrosion under environmental conditions. Depending on the film thickness, its porosity and its interactions with individual contaminants, an oxide-film can act as a diffusion barrier, a reactive barrier and/or as a molecular sieve hindering or lowering contaminant access to Fe^0 surfaces [50,53]. Therefore, mechanistic investigations regarding contaminant removal by Fe^0 materials should be accomplished under conditions favoring surface oxide-film generation and transformation [51]. On the contrary, the large majority of reported Fe^0 mechanistic results from batch experiments were achieved under well-mixed conditions. Under these experimental conditions, however, (i) Fe^0 dissolution is accelerated, yielding to more corrosion products which may adsorb contaminants or immobilize them during their transformation (e.g., precipitation, recrystallization). Thus, increased generation of corrosion products complicates mechanistic investigations; (ii) corrosion products precipitation (oxide-film formation) in the vicinity of Fe^0 surface is avoided or delayed since Fe^{II} transport away from the surface is accelerated; and (iii) chemical dissolution and mechanical abrasion of oxide-films is possible.

LOW REACTIVITY OF IRON METAL UNDER ENVIRONMENTAL CONDITIONS

Iron-based alloys for environmental remediation were originally introduced for the reduction of halogenated organic compounds [20, 21,54]. Initial encouraging results prompted researchers to extend their applicability to a large array of organic and inorganic compounds [12,15,55-57]. Thereby, key features characterizing the reactivity of Fe^0 materials under environmental conditions have been overseen. Three examples are given for illustration.

- Beside catalytic hydrogenation many reductive agents have been successfully used in the synthetic organic chemistry. The most classic and practical reductants are zinc (Zn^0), tin (Sn^0), and iron (Fe^0) [58]. However, the reactions with Fe^0 are performed in organic solvents or in aqueous acidic solutions (**statement 1**). This statement suggests that using Fe^0 materials for quantitative contaminant

reduction under environmental pH conditions ($6 \leq \text{pH} \leq 9$) is questionable.

- While using elemental metals in the synthetic organic chemistry, it is well-known that the reactivity of metallic zinc ($E^0 = -0.763 \text{ V}$) is superior to that of iron ($E^0 = -0.440 \text{ V}$) [46]. Therefore, to perform the reduction of some compounds (e.g., nitro compounds to amines) with Fe⁰, the reaction should be carried out at higher temperature [58] (**statement 2**). Statement 2 suggests that using Fe⁰ materials for quantitative contaminant reduction under ambient temperatures ($T < 30^\circ \text{C}$) is questionable.

- Because of the poor solubility of most organic compounds in water at ambient temperature, the remarkable properties of water near its critical point ($T_c = 374^\circ \text{C}$, $P_c = 221 \text{ bar}$) have prompted researchers to use it in organic synthesis [58,59]. There are increasing numbers of papers which suggest that near-critical water is an excellent solvent for organic reactions because organic reactions in it offer many advantages over those in traditional organic solvents or acidic aqueous solutions [59] (**statement 3**). Statement 3 corroborates the conclusions of statement 1 and 2.

Altogether statements 1 through 3 clearly show that direct quantitative organic contaminant reduction through Fe⁰ materials is not likely to occur. Additionally, working under critical conditions [58] or in acidic aqueous conditions has not univocally elucidated the real reaction mechanism (hydrogenation by H₂ or direct reduction by Fe⁰). Therefore, before proposing direct “reductive transformation” as the main pathway of organic compounds removal in Fe⁰/H₂O systems (under atmospheric conditions), the pioneers of the iron barrier technology should have brought clarity to the key issues of statements 1 and 2. Instead, the voluminous literature on Fe⁰ in the synthetic organic chemistry has been ignored. Even very well-documented results have been contradicted, one of the most important being without doubt the reported quantitative reduction of aromatic azo compounds by Fe⁰ materials [44,60,61]. This reaction (Béchamp reduction) was investigated more than 150 years ago by Antoine J. Béchamp [62] and is known to take place in a Fe⁰/HCl system [63].

Beside the low Fe⁰ reactivity under environmental conditions, inappropriate experimental conditions are other error sources in investigations regarding the processes of contaminant removal in Fe⁰/H₂O systems. The next section will present parameters influencing Fe⁰ reactivity and show how too large Fe⁰/contaminant molar ratios in combination with mixing operations may have created unrealistic reducing conditions.

INAPPROPRIATE EXPERIMENTAL CONDITIONS

Factors affecting Fe⁰ reactivity can be divided into three subgroups: (i) material-dependent factors (mostly not directly accessible to researchers), (ii) environment-dependent factors (investigable at individual relevant sites), and (iii) operational experimental parameters (should be designated to mimic environment-dependent factors).

Material-dependent factors include: manufacturing history of Fe⁰ materials, elemental composition of Fe⁰ materials (alloying elements: C, Cr, Mn, Ni, P, S, Si...), Fe⁰ particle size (nm, μm , mm), Fe⁰ surface area, and the oxidation state of the Fe⁰ surface [11,12]. Centuries of investigations on iron corrosion have not clarified the relative

importance of the individual factors [3,34,64,65].

Among environment-dependent factors, the following can be enumerated: water flow velocity, character of the generated oxide-film on Fe⁰ (composition, porosity, thickness), the ambient temperature, the water composition (major ions, co-contaminants), the availability of molecular oxygen (oxic vs. anoxic conditions), the nature of the contaminant. Environment-dependent factors are site specific and may significantly vary periodically (e.g., daily, seasonally). Their profound knowledge is indispensable for the rational choice of operational experimental parameters. For example, the hydrodynamics of the system should reflect the groundwater flow velocity. This condition is partly considered in designing column experiments [4], but is almost totally ignored in the design of batch experiments as discussed above [17,51].

Experimental operational parameters are fully determined by individual investigators. Ideally, their choice should always be rationalized by real situations or by the objective of individual experiments. These factors include [3,66-68] Fe⁰ preparation (e.g., acetone or acid wash), buffer application, the molar ratio of Fe⁰ to contaminant (Fe⁰ mass loading and initial contaminant concentration), volume of the bottles used in the experiment, volume of model solution added, mixing operations (bubbling, shaking, stirring), geometry of the reaction vessel, experimental duration or reaction time. Due to the lack of a unified procedure for conducting contaminant removal tests in Fe⁰/H₂O systems, different mechanisms for the same contaminant can be found in the literature [69,70].

From isolated sets of experiments, a huge number of variables (partly enumerated above) have been shown to affect aqueous Fe⁰ reactivity. This suggests that it is practically impossible to correlate data obtained with different natural waters (or synthetic solutions) on different Fe⁰ samples. Fortunately, however, while each of these factors is undoubtedly important under some particular set of conditions, there are wide ranges of conditions within which comparatively few variables have any large effect on Fe⁰ reactivity [36]. In particular, the main factors in the aqueous iron corrosion in natural waters are (i) the protectiveness of films of corrosion products, and (ii) the rate of oxidant diffusion (including H₂O, O₂, H⁺). Accordingly, any investigation of processes in Fe⁰/H₂O systems should be conducted under conditions favoring the formation and the transformation of oxide-films (e.g., in the mass transfer controlled regime). Ideally, this is obtained under stagnant conditions [51,71].

The discussion above reveals that the failure to consider Fe⁰/H₂O systems as a dynamic system consisting of the Fe⁰ material underlying a layer of corrosion products (oxide-film) is one of the major reasons why, despite two decades of intensive laboratory investigations, several aspects of contaminant removal from aqueous solutions in Fe⁰/H₂O systems are not really understood. Another important point is the Fe⁰/contaminant molar ratios. In synthetic organic chemistry, the used Fe⁰/educt molar ratios are rarely larger than 10 [29]: For example, Wang et al. [58] found that a ratio of nanosized iron metal to p-nitrotoluene of 3 : 1 was sufficient for satisfactory results (stirring conditions, 210°C and 2 h). In the reactive barrier literature Fe⁰/contaminant ratios up to 20,000 [29 and ref. therein] are used without justification and the solutions are mixed more or less strongly for hours or days.

While using inappropriate mixing operations and too large Fe⁰/contaminant ratios, reducing conditions may have been generated

and investigated by means of sophisticated experimental designs. These conditions are, however, irrelevant for natural systems. Moreover, geochemical models have been developed for contaminant removal in $\text{Fe}^0/\text{H}_2\text{O}$ systems while assuming reductive transformation at the Fe^0 surface [72].

DISCUSSION

It has been considered for almost two decades that the use of Fe^0 materials for groundwater remediation is based on scientific principles [73-76]. Thereafter, the suitability of Fe^0 materials for contaminant reductive removal is based on the low redox potential of the couple $\text{Fe}^0/\text{Fe}^{\text{II}}$, making Fe^0 a powerful reducing agent for many soluble contaminants [21,77]. But these considerations are proved unstable because the pioneer works on contaminant reductive removal by Fe^0 materials did not test and prove their theories by any scientific criteria [75,76]. In particular, the thermodynamics of hydroxide precipitation or Fe solubility were not properly considered (Fig. 1) [73]. Fortunately, contaminants are successfully removed in $\text{Fe}^0/\text{H}_2\text{O}$ systems by other processes [73,74]. The rational investigation of these processes and their optimization is a challenge for the scientific community [78,79].

The instable premise of direct contaminant reduction by Fe^0 materials, upon which the iron reactive barrier technology is based, has dragged a part of the environmental science community deeper into confusion during the past decade. For example, in their efforts to rationalize the removal of uranium (VI) from the aqueous phase in the presence of Fe^0 , Gu et al. [80] worked with clearly over-saturated U(VI) solutions (up to 10,000 mg/L or 0.042 M at near-neutral pH values) and reported that “results from the batch adsorption and desorption and from spectroscopic studies indicate that reductive precipitation of U on Fe^0 is the major reaction pathway.” Under their experimental conditions, however, U(VI) precipitation is thermodynamically and kinetically more favorable than the discussed mechanisms (adsorption and reduction). Clearly, all has been done to support the questionable premise. Here are three further examples: (i) very well-established scientific results have been contradicted (e.g., Béchamp reaction) [29]; (ii) contaminant co-precipitation with Fe^{II} and Fe^{III} species, which is the principle of flotation [81-86], has been ignored in order ‘to force’ direct reduction of metallic species to occur; (iii) the well-known “physical barrier” function of oxide-films has been transformed to that of “mediator of electron transfer” (electron-shuttle) from underlying Fe^0 to overlying contaminants (semiconductor and/or coordinating surface) in order to rationalize the hypothetical electron transfer from Fe^0 surface to dissolved oxidants [41].

The present work and related works [29,51,71,87] have presented a more simple and realistic model, acknowledging that quantitative contaminant removal primary occurs via adsorption or co-precipitation within the oxide-film. Depending on the availability of reductants and/or micro-organisms the contaminant may be further reduced, irrespective of the conductive properties of the oxide-film. This model is supported by the known adsorptive properties of iron oxides [39,88,89], and the fact that biological agents (viruses) [90], arsenic [91], and electrochemically non-reducible contaminants like Zn [92] are successfully removed from aqueous solution by Fe^0 materials (e.g. in $\text{Fe}^0/\text{H}_2\text{O}$ systems).

CONCLUDING REMARKS

The further development of Fe^0 bed filtration in general and the reactive wall technology in particular requires the use of appropriate experimental methodologies (e.g., no vigorous batch experiments). Available scientific results from two research areas must be properly exploited: (i) the results of investigations regarding passive film formation on Fe^0 in neutral and alkaline aqueous solutions. These investigations aimed at developing a detailed understanding of the film growth mechanisms, the film structure and composition, and the kinetics and mechanisms of reduction of iron oxides that form on the Fe^0 surface [93 and ref. therein], and (ii) the results of investigations regarding the polymerization of iron via hydrolysis yielding non-crystalline particles of key importance in the adsorption and transport of organic or inorganic pollutants [38,81].

Finally, the most important feature from the present communication is the solution of the existing vagueness for the design of Fe^0 beds [94]. In fact, determining an amount of Fe^0 and a bed thickness is no more dependent on a reductive reaction [2,95] but is solely a characteristic of water flow, water chemistry and Fe^0 intrinsic reactivity [96-98]. In other words, the profound understanding of the mechanism of contaminant removal in $\text{Fe}^0/\text{H}_2\text{O}$ systems has simplified bed design [96] and the Fe^0 bed is now proposed, or recognized, as an efficient material for decentralized safe drinking water production [97-100]. Intensive research on several fronts is needed to transform this vision into reality.

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