On the suitability of admixing sand to metallic iron for water treatment

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Abstract

This communication clarifies the relationships between sand addition and the sustainability of iron/water systems for environmental remediation. It is shown that any enhanced contaminant removal in an iron/sand/water relative to an iron/water system is related to the avoidance/delay of particle cementation by virtue of the inert nature of sand. The argument that sand dissolution produces protons (H+) to sustain iron corrosion is disproved by the very low dissolution kinetics solubility of SiO2-bearing minerals under environmental conditions. This demonstration corroborates the concept that aqueous contaminant removal in iron/water systems is not a process mediated by electrons from Fe0.

Keywords: Adsorption, Co-precipitation, Dissolution kinetics, Sand admixture, Zerovalent iron.
1. Introduction

The use of metallic iron (Fe$^0$) has become an established technology for environmental remediation and water treatment in recent years (O’Hannesin and Gillham, 1998; Odziemkowski and Simpraga, 2004; Bartzas et al., 2006; Li et al., 2006; Henderson and Demond, 2007; Hussam and Munir, 2007; Hussam, 2009; Noubactep et al. 2009a; O et al., 2009; Bartzas and Komnitsas, 2010; Li and Benson, 2010; Comba et al., 2011; Gheju, 2011; Gunawardana et al., 2011; Jeen et al., 2011; Allred, 2012; Ingram et al., 2012; Jeen et al., 2012; Huang et al., 2012; Noubactep et al., 2012a; Ruhl et al., 2012a; Ruhl et al., 2012b; Ruhl et al., 2012c). The processes governing contaminant removal are considered widely understood (Cong et al., 2010; Henderson and Demond, 2011; ITRC, 2011; Chen et al. 2012a; Jeen et al., 2012; Huang et al., 2013a; Huang et al., 2013b). Meanwhile, reported studies are focused on ways to enhance the Fe$^0$ reactivity such as using nano-sized particles and bimetallic systems (Ghauch et al., 2011; Crane and Scott, 2012; Noubactep et al., 2012a), using other reactive metallic elements (e.g. Al$^0$, Ti$^0$, Zn$^0$) (Bojic et al., 2007; Sarathy et al., 2010; Guo et al., 2012; Lee et al., 2012; Salter-Blanc et al., 2012) or using hybridized systems like Fe$^0$/Fe$_3$O$_4$/Fe$^{II}$ (Huang et al., 2012; Huang et al., 2013a; Huang et al., 2013b). However, the validity of the current paradigm has been seriously questioned as the relevance of direct reduction (reduction by electrons from Fe$^0$) for observed efficiency of Fe$^0$/H$_2$O systems was challenged (Lavine et al., 2001; Noubactep, 2007; Noubactep, 2008; Jiao et al., 2009; Ghauch et al., 2010; Noubactep, 2010a; Noubactep, 2010b; Ghauch et al., 2011; Gheju and Balcu 2011; Noubactep, 2011a; Noubactep, 2011b; Noubactep, 2012a; Liu et al., 2013). The problem is well worthy to be discussed further. The present contribution focuses on the use of sand as additive material in Fe$^0$ filtration systems.

The idea that sand/quartz (SiO$_2$) admixture enhances the extent/efficiency of contaminant removal in Fe$^0$/H$_2$O systems has significant support in the literature (Powell et al., 1995; Kaplan and Gilmore, 2004; Song et al., 2005; Wu et al., 2005; Guo et al., 2011). This idea co-
exists with concerns that SiO₂ addition is a ‘dilution’ of reactive materials and is necessarily accompanied by slower kinetics and lower extent of the decontamination process (Devlin and Patchen, 2004; Bi et al., 2009; Ruhl et al. 2012a). Each of this argument is seemingly supported by strong experimental evidence and has let to the recent statement that “there is no conclusive evidence that a sand/iron mix is better or worse than a pure iron barrier” (Ulsamer, 2011). Moreover, although the efficiency of Fe⁰ PRBs was demonstrated with a 22:78 Fe⁰:sand w/w mixture for the removal of TCE (O’Hannesin and Gillham, 1998), Ruhl et al. (2012a) recently demonstrated the inefficiency of dual Fe:additive mixtures for the removal of the same compound (e.g. TCE) from a contaminated groundwater. Tested additives included anthracite, gravel, pumice and sand.

The objective of this paper is to clarify the impact of sand addition on the long term efficiency (or sustainability) of Fe⁰/H₂O systems using a mathematical modelling. The discussion starts by a careful analysis of the Fe⁰/sand/H₂O system on a pure chemical perspective.

2. The chemistry of the Fe⁰/sand/H₂O system

The presentation in this section is limited to an ideal anoxic system (absence of oxygen). Under such conditions Fe⁰ is oxidized by protons (H⁺) from water dissociation after Eq. 1:

\[
\text{Fe}^0 + 2 \text{H}^+ \Rightarrow \text{Fe}^{2+} + \text{H}_2
\]  

After the Lechatelier’s Principle, Eq. 1 is sustained/enhanced in a system if: (i) H⁺ is produced, (ii) Fe²⁺ is consumed and (iii) H₂ is consumed or escapes out of the system.

Is the view that sand sustains the efficiency of Fe⁰ supported by Lechatelier’s Principle? It is obvious that sand is not a reservoir of H₂. Accordingly, H₂ may escape or be used for microbial activities. Sand may potentially adsorb Fe²⁺ but its adsorption capacity is limited and any redox reaction of adsorbed Fe²⁺-species is only indirectly coupled with the parent Fe⁰.

The last discussed option is that sand may produced protons. The ability of sand to produce protons has been documented in the Fe⁰ literature (Powell et al., 1995; Blowes et al., 1997; Powell and Puls, 1997). In this context a ‘buffering effect’ of SiO₂-bearing materials has been
reported. However, because of the very slow rate of SiO$_2$ dissolution (Rimstidt and Barnes, 1980; Kehew, 2001), it is doubtful whether any significant acidification by SiO$_2$ dissolution may occur (Eq. 2). The observed pH decrease in short-term batch experiments can be attributed to hydrodynamic effects (mixing operations) dissolving weathered fines from the surface of used materials. After this initial dissolution observed in Batch experiments, no quantitative SiO$_2$ dissolution could be expected at pH $\geq$ 4.5.

$$\text{SiO}_2(s) + 2 \text{H}_2\text{O} \rightarrow \text{H}_4\text{SiO}_4(aq) \quad (2)$$

The presentation until now shows that sand admixture cannot actively sustain the efficiency of Fe$^0$/H$_2$O systems in the long-term. Therefore, the observed enhanced efficiency (Song et al., 2005; Bi et al., 2009; Gottinger et al., 2010) should be explained by other processes.

3. The operating mode of Fe$^0$/sand/H$_2$O

3.1 Descriptive aspects

Sand is a geo-material conventionally used for water treatment (Darcy, 1856; Weber-Shirk and Dick, 1997; Ngai et al., 2007; Kubare and Haarhoff, 2010; Gottinger et al., 2011). Sand is mostly considered a non-reactive material for media filtration. In some cases, this material is mixed with reactive natural materials to sustain selective removal of some species (Yao et al., 1971; Ali, 2012). Tested natural reactive materials include iron ores (e.g. siderite, hematite), manganese ores, volcanic stones, and zeolites (Guo et al., 2007a; Guo et al., 2007b; Doula, 2009). In other cases, sand is artificially coated with reactive media such as iron or manganese oxides (Gupta et al., 2005). While filtration on pure sand bed is termed ‘media filtration’ (size-exclusion of suspended particles), adsorption on coated sand is known as ‘adsorptive filtration’ (Edwards and Benjamin, 1989; Dermatas and Meng, 2004). This classification is operational as sand may adsorb some species more strongly than iron oxides. A classical example was reported by Mitchell et al. (1955). These authors demonstrate that some iron oxide coated sands are worse adsorbents for methylene blue than original materials (non-coated). The observation of Mitchell et al. (1955) is very important for the design of Fe$^0$...
filtration systems. In fact, species that are not readily removed by iron oxide coated sand should be removed before the Fe\(^0\)-containing zone, for instance on a granular carbon or sand layers. For the purpose of this communication it is sufficient to consider that in a Fe\(^0\)/sand/H\(_2\)O system, iron-oxide-coated sand is generated in-situ.

Previous theoretical studies have argued that a Fe\(^0\)-containing zone must be situated after one or several biosand filters to operate under anoxic conditions where less expansive corrosion products are generated (Noubactep et al., 2009a; Noubactep, 2010c; Noubactep and Caré, 2010; Noubactep and Schöner, 2010; Noubactep et al., 2010; Noubactep et al. 2012b; Noubactep et al. 2012c). Methylene blue can be regarded as proxies for all species with low adsorptive affinity to iron oxides. This observation of Mitchell et al. (1955) corroborates the view that, in a multi-barriers system, a Fe\(^0\)-containing zone must never be implemented at the beginning of the chain. Moreover, the fact that methylene blue is quantitatively removed in Fe\(^0\)/sand systems (Noubactep, 2009; Chen et al., 2012b; Miyajima and Noubactep, 2012; Btakteu et al., 2013; Miyajima and Noubactep, 2013) confirms that adsorption, co-precipitation and enhanced size-exclusion are the fundamental mechanisms of contaminant removal in Fe\(^0\)/H\(_2\)O systems. Accordingly, despite the low affinity of MB for adsorbing species in Fe\(^0\)/H\(_2\)O systems, quantitative MB removal can be achieved upon proper system design (Btakteu et al., 2013). Recent calculations have demonstrated that using the same mass of Fe\(^0\), the best treatment system is achieved in using the column with the smallest diameter (Noubactep et al. 2012c). In such beds/columns Fe\(^0\) is mixed with a non expansive material, e.g. sand. The most favourable Fe\(^0\) volumetric proportions are bellow 50 % (Miyajima, 2012; Miyajima and Noubactep, 2013), but the intrinsic reactivity of Fe\(^0\) and the relative geometry of Fe\(^0\) and sand should be considered as well (O et al., 2009; Caré et al. 2012, Btakteu et al. 2013). It is hoped that all these aspects will be considered in future system design.

### 3.2 Sand as dispersant
Aqueous iron corrosion at pH > 4.5 is a cycle of (i) oxidative dissolution ($Fe^0 \rightarrow Fe^{2+}$), (ii) solvatation ($Fe(H_2O)_6^{2+}$), (iii) volumetric expansion (formation of $Fe(OH)_n$ colloids), (iv) volumetric contraction ($Fe$ hydroxides/oxides) processes. The overall process is known as ‘volumetric expansion’ (Noubactep, 2010c; Noubactep and Schöner, 2010; Noubactep, 2011c). The volume of any iron $Fe$ hydroxide or oxide is higher than that of the original metal ($Fe^0$) (Pilling and Bedworth, 1923; Caré et al., 2008). The ratio between the volume of expansive corrosion product and the volume of iron consumed in the corrosion process is called ‘rust expansion coefficient’. However, this coefficient does not reflect the intermediary expansive stage of the process which yield volumetric colloids that are capable of enmeshing foreign species during their further transformation to oxides (Noubactep, 2010a; 2010c; 2011c, 2012a). More importantly, these volumetric colloids have the ability to ‘cement’ or ‘compact’ granular particles (Mackenzie et al., 1999; Kaplan and Gilmore, 2004). The cementation process results in limited access to all three potential removing agents: non corroded $Fe^0$, iron oxides and sand. Thus contaminant removal by adsorption and/or coprecipitation is inhibited. On the contrary, in fest bed filtration systems, adsorptive size-exclusion is enhanced but the system permeability is reduced (permeability loss). This is the first reason why pure $Fe^0$ systems (100 % $Fe^0$) are efficient but not sustainable (Hussam, 2009; Noubactep et al., 2010).

Regarding $Fe^0$ particles as ‘cement generators’ suggests that the first tool to limit cementation/compaction is to decrease the proportion of $Fe^0$ (Caré et al., 2012; Noubactep et al., 2012b). In other words, batch and column systems with 100 % $Fe^0$ leave no room for solid phase expansion (Miyajima and Noubactep, 2012). Such systems will ‘clog’ rapidly and iron corrosion and the corresponding contaminant removal will be minimal. In other words, sand and other non expansive additives should not be regarded as material slowing the mass transport of reactants to the $Fe^0$ surface but rather as a dispersant sustaining the system’s efficiency (more $Fe^0$ is consumed, more adsorbing agents are produced) (Noubactep et al.,
The use of non-reactive materials to sustain Fe\(^{0}\) efficiency is current at nano-scale (Gheju, 2011; ITRC, 2011; Crane and Scott, 2012; Noubactep et al., 2012a). On the other hand, the efficiency of the hybridized Fe\(^{0}/Fe_{3}O_{4}/Fe^{II}\) presented by Huang et al. (2012; 2013a; 2013b) can be attributed to the non/less expansive nature of Fe\(_{3}O_{4}\) (magnetite) and the enhanced reactivity of Fe\(^{II}\) adsorbed onto magnetite and nascent iron hydroxides (Charlet et al., 1998; Liger et al., 1999; Noubactep, 2007; Noubactep, 2008; Noubactep, 2011a).

Regarding sand and other non-expansive additives as useful tools to sustain Fe\(^{0}\) efficiency explains all reported discrepancies on the effect of sand addition on the efficiency of Fe\(^{0}/H_{2}O\) systems. In particular, the statement of Ulsamer (2011) that “there is no conclusive evidence that a sand/iron mix is better or worse than a pure iron barrier” is due to the fact that results have been compared with little care on the operational conditions of their production (Crane and Noubactep, 2012; Noubactep, 2012b). Additionally, there is still no index to characterize the intrinsic reactivity of Fe\(^{0}\) material (Noubactep et al., 2009b; Miyajima and Noubactep, 2012; Btatekeu et al., 2013; Miyajima and Noubactep, 2013). For example, a filtration system (e.g. a column) containing 100 % of a less reactive material (material A) may not experience clogging while a readily reactive material (material B) could induce clogging even at 40 % volumetric proportion within similar working conditions. In other words, the suitability of admixing additive to iron can not be accessed before the intrinsic reactivity is properly characterized. Beside the Fe\(^{0}\) intrinsic reactivity, other relevant factors influencing the porosity of filtration beds should be considered (Kubare and Haarhoff, 2010; Caré et al., 2012; Btatekeu et al., 2013; Miyajima and Noubactep, 2013). Factors influencing the efficiency of Fe\(^{0}\) filtration systems include: (i) the particle size and form of reactive materials, (ii) the dimensions of the treatment systems and (ii) the chemistry of raw waters (Noubactep et al., 2012c; Caré et al., 2012; Crane and Noubactep, 2012; Ruhl et al., 2012b; Togue-Kamga et al., 2012a, Togue-Kamga et al., 2012b; Btatekeu et al., 2013; Miyajima and Noubactep, 2013).
4. Discussing the process of permeability loss in Fe\(^0\)/H\(_2\)O systems

In this section, an evaluation of permeability loss in a series of filters (e.g. reactive zones) with an initial pore volume \(V_p = 100 \text{ mL}\) is given. Assuming an initial porosity of 40 % the volume of the filter is \(V_{rz} = 250 \text{ mL}\) and the volume of solid is \(V_{\text{solid}} = 150 \text{ mL}\). This volume can be occupied by 1170 g of granular Fe\(^0\) (density: 7.8 g/cm\(^3\)). It is assumed that this filter is used to (electro)chemically reduce CrO\(_7^{2-}\) to Cr\(^{3+}\) (Eq. 1) which is then precipitated as Cr\(_2\)O\(_3\) (unit cell volume: 289.85 Å\(^3\) corresponding to 174.6 mL/mol) (Prewitt et al., 1969) under anoxic conditions (Fe\(_3\)O\(_4\) is the major iron corrosion product).

\[
3 \text{ Fe}^0 + \text{ Cr}_2\text{O}_7^{2-} + 14 \text{ H}^+ \rightarrow 3 \text{ Fe}^{2+} + 2 \text{ Cr}^{3+} + 7 \text{ H}_2\text{O}
\]  

(1)

The initial pore volume \((V_p = 100 \text{ mL})\) is completely filled when 570 g of Fe\(^0\) (10.17 moles) is oxidized and precipitated as Fe\(_3\)O\(_4\). Accordingly, using a 100 % Fe\(^0\) bed corresponds to a 51.3 % material wastage with the additional disadvantage that the system is not sustainable. Assuming that Fe\(^0\) oxidation is coupled to chemical Cr\(^{VI}\) reduction (Eq. 1), the initial pore volume is filled by only 0.57 mole of Cr\(_2\)O\(_3\). This corresponds to the oxidation of 1.72 moles of Fe\(^0\) (by 0.57 mole of Cr\(_2\)O\(_7^{2-}\)). 0.57 mole is contained in 29,640 L of a 1 mg/L Cr\(_2\)O\(_7^{2-}\). In other words, up to 30 m\(^3\) of water containing 1 mg/L Cr\(_2\)O\(_7^{2-}\) can be treated by only 600 g (0.6 kg) of Fe\(^0\). These calculations corroborate the huge potential of Fe\(^0\)/H\(_2\)O systems for water treatment while disapproving the current expression of the removal capacity (in mg contaminant per g Fe\(^0\)) partly derived from batch experiments.

Summarized, \(V_p = 100 \text{ mL}\) is completely clogged when (i) 10.17 moles of Fe\(^0\) is oxidized by water and subsequently precipitated as Fe\(_3\)O\(_4\) or (ii) 1.72 moles of Fe\(^0\) is oxidized by 0.57 mole Cr\(_2\)O\(_7^{2-}\) to form 0.57 mole of Cr\(_2\)O\(_3\). However, it should be kept in mind that Cr\(_2\)O\(_7^{2-}\) can be removed without reduction and corrosion products are always oxides/hydroxides mixtures.

4.1 Permeability loss resulting from expansive corrosion

The methodology for the assessment of the permeability loss is explicitly presented in Caré et al. (2012). Fe\(^0\)/sand systems with Fe\(^0\) volumetric ratios (\(\tau_{\text{ZVI}}\)) varying from 0 to 100 % are
considered. A Fe$^0$ filter is made up of granular solid materials (Fe$^0$, sand) and the voids between the grains (pore volume, $V_p$). The volume of the reactive zone is given by (Eq. 2):

$$V_{rz} = V_{ZVI} + V_{sand} + V_p$$  \hspace{1cm} (2)

Ideally, a reactive zone is clogged when $V_p$ is completely filled with retained solutes, suspended particles and/or in-situ generated species. However, clogging is usually observed only at the entrance zone of Fe$^0$ systems (Mackenzie et al., 1999; Kaplan and Gilmore, 2004; O et al., 2009).

Upon oxidative dissolution and subsequent precipitation, the volume of each corrosion product (e.g. Fe$_3$O$_4$; $\eta = 2.08$) is higher than that of the original metal (Pilling and Bedworth, 1923). The excess volume contributing to system clogging is given by $V_{\text{excess}}$ in Eq. 3 (Caré et al., 2012).

$$(\eta - 1) * \tau_{ZVI} * V_{\text{solid}} = V_{\text{excess}}$$  \hspace{1cm} (3)

Where $\tau_{ZVI}$ ($0 \leq \tau_{ZVI} \leq 1$) is the volumetric fraction of metallic iron relative to the solid phase in the bed or the reactive layer.

The Fe$^0$ filtration system is clogged when the volume $V_{\text{excess}}$ is equal to the initial inter-granular voids ($V_p$).

$$(\eta - 1) * \tau_{ZVI} * V_{\text{solid}} = V_p$$  \hspace{1cm} (3a)

Eq. 4 suggests that, for every $\eta$ value (i.e. every oxide), $V_p$ is a linear function of $\tau_{ZVI}$ (Fig. 1). Negative values of $V_p$ are not considered as they have no physical meaning. In other words, $V_p < 0$ indicates an excess of Fe$^0$ and system clogging occurred before complete Fe$^0$ depletion.

### 4.2 Contaminant accumulation and permeability loss

The calculations in this work consider solely the initial state (Fe$^0$) and the final state (Fe$_3$O$_4$). The kinetics of the corrosion reaction is difficult to access. In the oil industry, the corrosion rates of external line pipe are expected to be $< 10 \mu\text{myr}^{-1}$ but could increase to up to 700
μmyr\(^{-1}\) in the presence of sulfate reducing bacteria (Sherar et al., 2011). In the Fe\(^0\) remediation industry, no such experience-based guide values have been published. The paramount factors determining the corrosion kinetics include: (i) the intrinsic reactivity of Fe\(^0\) materials, (ii) the water chemistry (pH, dissolved O\(_2\), nature and extent of contamination) and (iii) water flow rate.

In this section, the occupation of the pore volume by removed Cr (as crystalline Cr\(_2\)O\(_3\)) is discussed. The evolution of a system initially containing 50 % Fe\(^0\) (τ\(_{ZVI}\) = 0.5) is characterized as the extent of Fe\(^0\) depletion (α\(_{ZVI}\)) varies from 0 to 100 %. It is assumed that corrosion products results solely from Fe\(^0\) oxidation by Cr\(^{VI}\) (Fe\(^0\):Cr\(^{III}\) = 3:2 or Fe\(^0\).Cr\(_2\)O\(_3\) = 3:1).

Fig. 2 summarizes the results and shows unambiguously that porosity loss due to pore filling with insi-situ generated corrosion products is significant. While considering the pore occupation by Cr\(_2\)O\(_3\) it is seen that \(V_p\) is completely clogged when only 5 % of the initial amount of Fe\(^0\) has reacted with Cr\(^{VI}\) to form crystalline Cr\(_2\)O\(_3\). Considering Fe\(_3\)O\(_4\) alone, complete clogging occurred when about 75 % of the initial amount of iron is consumed. This conclusion seem to underscore the impact of iron corrosion products in filling the initial porosity. However, one should remember that water oxidizes Fe\(^0\) and contaminants are present in trace amounts (Henderson and Demond, 2011; Kümmerer, 2011). Iron oxides certainly quantitatively precipitate (at pH > 5.0). In other words, the calculated volume occupation by Fe\(_3\)O\(_4\) is very conservative and even unrealistic because strict stoichioimetric reduction by Fe\(^0\) has never been reported (Gould et al., 1982). In other words, stoichoimetric Cr\(^{VI}\) reduction by Fe\(^0\) is unlikely to occur under environmental conditions. Fig. 2 presents the line for a reaction efficiency of 33 % meaning that for 3 moles of dissolved Fe\(^{2+}\), ‘only’ one mole induces Cr\(^{VI}\) reduction. In this case, system clogging is observed just at 20 % Fe\(^0\) consumption.

The last important issue from Fig. 2 is the representation of the percent consumption of Fe\(^0\).

At α\(_{ZVI}\) = 0, the system behaves like a pure sand filter. As α\(_{ZVI}\) increases, the efficiency of the
System virtually increases. \( \text{Fe}^0 \) corrosion stops when the residual porosity is zero. Fig. 2 shows clearly that any \( \text{Fe}^0 \)-amended sand filter, has to find a compromise between (i) increased efficiency by virtue of the \( \text{Fe}^0 \) reactivity and (ii) reduced porosity as result of expansive iron corrosion. Fig. 2 suggests that for a system containing 50 % (vol/vol) \( \text{Fe}^0 \), and working under anoxic conditions, this optimum system is around 40 %. Given the difference in density between \( \text{Fe}^0 \) (7.8 g cm\(^{-3}\)) and sand (2.6 g cm\(^{-3}\)) the corresponding weight ratio is necessarily lower than 1:1 (50 % w/w) which has been commonly tested and used (Miyajima, 2012). In other words, suitable \( \text{Fe}^0 \)/sand systems are yet to be tested. However, it is certain that enhanced contaminant removal in \( \text{Fe}^0 \)/sand/H\(_2\)O relative to \( \text{Fe}^0 \)/H\(_2\)O systems is related to the delay of particle cementation by virtue of the inert nature of sand.

5. Concluding remarks

Decrease of the hydraulic conductivity (permeability loss) in \( \text{Fe}^0 \) filtration systems has not been attributed to volumetric expansive iron corrosion. The calculations presented here demonstrate that gas (H\(_2\)) evolution and foreign solid precipitation may not be responsible for the majority of permeability loss (Fig. 2). The kinetics and the extent to which permeability loss occurs at a given site depends both on the intrinsic reactivity of used \( \text{Fe}^0 \) and on the water chemistry. However, it is certain that pure \( \text{Fe}^0 \) filtration systems are not sustainable as little room is left for iron corrosion (volumetric expansion). Accordingly, any argumentation that sand addition avoid the passivation of the \( \text{Fe}^0 \) surface or acts as buffering agent thanks to production of silicic acid is faulty. This evidence can only be acknowledged when the whole \( \text{Fe}^0 \) remediation community has considered the overall theory of the system. Without a theory of the system, new data will be produced but significant advance in knowledge will not be achieved.

An essential prerequisite for the universal acceptance of \( \text{Fe}^0 \) as a remediation technology is a fundamental understanding of processes occurring in \( \text{Fe}^0 \)/H\(_2\)O systems. The introduction of this promising technology was based on a false explanation of good experimental
observations. The original error was identified and widely presented in the international literature since 2007. The scientific community has not yet dealt with the issue and is presently virtually divided into two schools: pro and contra “reductive transformation” or “adsorption, co-precipitation, size-exclusion”. However, the latter concept was clearly presented as a revision of the former. The long-lasting sterile discussion should stop now and efforts should focus on developing the chemistry free $\text{Fe}^0$ technology.

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Figure 1

![Graph showing various iron oxides and hydroxides with corresponding volume percentages and ZVI concentration.](image)
Figure 2

![Graph showing the relationship between Χ [%] and ζ [%] for different PL and Fe oxidation conditions.]

- PL (Fe₃O₄)
- PL (3 Fe₃O₄)
- PL (Fe₃O₄ + Cr₂O₃)
- ΖVII oxidation

Axes:
- X [%] on the y-axis
- ζ [%] on the x-axis

Legend:
- Open circles for PL (Fe₃O₄)
- Triangles for PL (3 Fe₃O₄)
- Stars for PL (Fe₃O₄ + Cr₂O₃)
- Closed circles for ΖVII oxidation
Figure Caption

**Figure 1:** Evolution of the residual porosity ($V_p$) as function of the Fe$^0$ volumetric ratio ($\tau_{ZVI}$) in the reactive zone for various iron corrosion products. It is seen that Fe$^0$ ratios $> 60 \%$ are pure material wastage. The more sustainable systems are those working under anoxic conditions (Fe$_3$O$_4$ as major corrosion product).

**Figure 2:** Evolution of the porosity loss (PL) and the theoretical extent of iron oxidation as function of the % consumed Fe ($\alpha_{ZVI}$) in an anoxic system initially containing 50 % Fe$^0$ particles (and 50 % quartz). It is assumed that Fe$^0$ is oxidized solely by Cr$_2$O$_7^{2-}$ and produce crystalline Cr$_2$O$_3$. PL is due both to pore filling by Cr$_2$O$_3$ and Fe$_3$O$_4$. In one case an efficiency of 33 % is assumed (3 Fe$_3$O$_4$).