

A CRITICAL REVIEW ON THE PROCESS OF CONTAMINANT REMOVAL IN Fe⁰-H₂O SYSTEMS

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Abstract

A central aspect of the contaminant removal by elemental iron materials (Fe⁰ or Fe⁰-materials) is that reduction reactions are mediated by the iron surface (direct reduction). This premise was introduced by the pioneers of the reactive wall technology and is widely accepted by the scientific community. In the meantime enough evidence has been provided to suggest that contaminant reduction through primary corrosion products (secondary reductants) do indeed occur (indirect reduction). It was shown for decades that iron corrosion in the pH range of natural waters (4-9) inevitably yields an obstructive oxide-film of corrosion products at the metal surface (oxide-film). Therefore, contaminant adsorption onto corrosion products and contaminant co-precipitation with corrosion products inevitably occurs. For adsorbed and co-precipitated contaminants to be directly reduced the oxide-film should be electronic conductive. This study argues through a literature review a series of points which ultimately lead to the conclusion that, if any quantitative contaminant reduction occurs in the presence of Fe⁰-materials, it takes place within the matrix of corrosion products and is not necessarily a direct reduction. It is concluded that Fe⁰-materials act both as source of corrosion products for contaminant adsorption/ co-precipitation and as a generator of Fe^{II} and H₂ (H) for possible catalytic contaminant reduction.

Keywords: Adsorption, Co-precipitation, Elemental Iron, Groundwater, Remediation.

INTRODUCTION

The advent of readily available and of low-cost elemental iron materials (Fe^0 -materials) in the water treatment (mostly groundwater remediation and wastewater treatment) has resulted in the use of materials from various origin [1-5]. Different classes of organics and inorganic compounds have been successfully removed from the aqueous phase in the presence of Fe^0 -materials [1, 6-15]. The earliest detailed surveys involving contaminant removal by Fe^0 -materials in laboratory batch systems raised speculations that the decontamination occurs through a reduction reaction at the surface of the metal [16-20]. In the meantime several other reductants (secondary reductants) have been identified in the system Fe^0 - H_2O including green rust, structural Fe^{II} , and atomic or molecular hydrogen [21-23]. Therefore contaminant reduction can also occur within the matrix of corrosion products.

To rationalise the hypothesis of contaminant removal at the surface of Fe^0 -materials, the Fe^0 surface was arbitrarily divided into two types of sites: “reactive” and “non-reactive” sites [24]. Thereafter, reactive sites are those where the chemical/electrochemical reaction takes place, while on non-reactive sites only sorption interactions occur. This segregation implicitly neglects the fact that “reactive” sites readily react with water such that they should be covered with an oxide-film immediately after immersion [25]. The effects of oxide-film growth on contaminant transport to the Fe^0 surface has not been properly investigated. Background knowledge in this area comes primarily from two fields: (i) atmospheric and immersed corrosion [26-30], (ii) subsurface pipe corrosion [31-34].

It should be acknowledged that, several studies investigated the role of iron corrosion products on the process of contaminant removal in Fe^0 - H_2O systems [35-40]. However, the objective of the investigators was mostly to explain the role of the film in mediating direct contaminant reduction

in $\text{Fe}^0\text{-H}_2\text{O}$ systems. Clearly direct reduction has been accepted as main reaction path and the overall reaction proposed in the seminal work of Matheson & Tratnyek [19] is still valid. The failure to generally consider adsorption, co-precipitation and indirect reduction as possible independent contaminant removal pathways is likely one of the major reasons why despite a decade of intensive research, the real contaminant removal mechanisms have not yet been completely elucidated [10, 41]. There are two more facts suggesting that the importance of the oxide-film on Fe^0 is not properly addressed: (i) experiments are conducted with acid pre-washed Fe^0 -materials or in the presence of ligands (EDTA) to free the Fe^0 surface from corrosion products or avoid their formation [19, 42, 43]; (ii) in modeling the process occurring in $\text{Fe}^0\text{-H}_2\text{O}$ systems, the specific surface area of the used Fe^0 -material is used. For example, the commonly applied surface-area-normalized kinetic model to contaminant reduction in Fe^0 batch systems assumes that the rate of reaction between iron and a contaminant is first-order with respect to both total iron surface area and contaminant concentration [44]. However, the Fe^0 surface is not accessible as a rule.

It is the objective of this study to: (i) recall that in the pH range of natural waters the Fe^0 surface is always covered by corrosion products, and (ii) qualitatively present chemical, electrochemical, and transport processes occurring simultaneously in a $\text{Fe}^0\text{-H}_2\text{O}$ system. From this presentation a discussion of the spatial location of eventual quantitative contaminant reduction will be deduced. The process of aqueous iron corrosion will be first presented.

THE PROCESS OF AQUEOUS IRON CORROSION

A voluminous literature exists on the corrosion of iron and steel, which are currently used as Fe^0 -materials for water treatment. One can be overwhelmed by the huge number of factors that have

been reported to affect the rate of aqueous iron corrosion under immersed conditions (solution pH, temperature, impurities in the metal, aqueous iron concentration, flow velocity, character of the oxide-films on iron, salt content of the water, presence of oxidizing or passivating agents, etc.). However, the main factors in the aqueous iron corrosion in natural waters are the protectiveness of films of corrosion products and the rate of oxidant (e.g. O_2 , H^+) diffusion across the film [27, 30, 45-48].

Aqueous iron corrosion occurs by two different mechanisms: chemical and electrochemical oxidation. Even though aqueous chemical iron oxidation [26, 49-51] can not be excluded under immersed conditions, aqueous iron corrosion (e.g. in reactive walls) is generally agreed to occur through an electrochemical mechanism [19, 29, 34, 52, 53]. The concept of electrochemical corrosion has been described in the context of the reactive wall technology (19, 53) and will not be repeated here. The essential features in this regard are (i) the electrolyte (contaminated water), (ii) an anode and a cathode, (iii) the passage of electrons through the external (metallic) circuit (from anode to cathode), (iv) the passage of ions through the electrolyte, (v) the corrosive attack at the anode, where Fe^{2+} ions enter into the solution (leaving the metal negatively charged with excess of electrons), (vi) the protective effect at the cathode, where hydrogen ions for example are discharged (electrons being given up from the metal). All these features find their counterpart in ordinary immersed corrosion, even though separate anodes and cathodes cannot always be distinguished visually. Therefore, aqueous iron corrosion can be regarded as to be made up of anodic and cathodic components. The anodic process is the iron dissolution (Eq. 1, table 1). Depending on the cathodic process, two main types of aqueous iron corrosion have been described: (i) hydrogen evolution type (Eq. 4, table 1) and (ii) oxygen absorption type (Eq. 8, table 1).

Hydrogen evolution corrosion

The characteristic feature of "hydrogen evolution corrosion" is the liberation of hydrogen as hydrogen gas (H_2) at the cathode. Hydrogen evolution corrosion is normally associated with acid electrolytes (e.g. acid mine drainage) and is promoted by two key factors: the conductivity and the pH of the contaminated water [26]. Therefore, the rate at which fresh acid (H^+) can diffuse to the metal surface is a possible controlling factor for hydrogen evolution corrosion. Assuming that there is no falling off in the supply of acid, the controlling factor is commonly supplied by the development of an obstructive film (of hydrated oxides) at either the anode or the cathode. In the hydrogen evolution corrosion it is rare to have an obstructive film at the anode, since iron oxides or hydroxides are normally soluble in acid electrolytes. Most frequently, the obstruction occurs at the cathode and is associated with the complex phenomenon of "hydrogen overpotential", whereby the transition of electrically discharged hydrogen ions (H^+) to the molecular condition (H_2) is to a greater or lesser extent suppressed. This "cathodic polarization" constitutes by far the commonest controlling factor under conditions of hydrogen evolution corrosion [29]. Since natural waters are generally of near neutral pH, corrosion with oxygen absorption is more interesting for the discussion in this paper.

Corrosion with oxygen absorption

The oxygen absorption type of immersed iron corrosion is characteristic of neutral waters. Electrons leave the cathode through the intervention of oxygen (oxygen reduction - Eq. 8). Thus the presence of oxygen prevents "cathodic polarization" by disposing of electrons that would otherwise accumulate in the cathode. Since oxygen absorption corrosion occurs in neutral waters

where iron solubility is very low, there is clearly a much greater chance of obstructive films forming at the anode. This film acts as a diffusion barrier for oxygen supply which is essential for the mechanism to continue [27-29, 54].

Implications for Fe⁰ reactive walls

The main conclusion from this literature survey on the process of aqueous iron corrosion is that iron corrosion at near neutral pH values ($4 \leq \text{pH} \leq 9$) yields an obstructive surface film that controls the rate of oxygen supply and may suppress corrosion in the long term. This conclusion is very important for the use of Fe⁰-materials in the groundwater remediation. In fact, while using Fe⁰-materials in the subsurface remediation (mostly under nearly anoxic conditions), it is assumed that electro-active contaminants will (initiate and) sustain iron corrosion in the same way as molecular oxygen as discussed above. However, any contaminant of interest must migrate across the oxide-film. Therefore, the structure of the oxide-film (e.g. composition, porosity, thickness, surface groups) and the nature of the contaminant (size, chemical nature, affinity to oxide-film) are to be considered when discussing the mechanism of contaminant removal in Fe⁰-H₂O systems. For this purpose, investigations should be conducted under conditions favouring the development of an oxide-film at the Fe⁰ surface. Instead, the vast majority of experiments have been conducted under mixing (bubbling, shaking, stirring) conditions [41]. Under mixing conditions, however, iron corrosion is accelerated and the formation of the oxide-film at the Fe⁰ surface is disturbed [55-57]. In fact, mixing Fe⁰-H₂O systems is mostly considered as an important tool to facilitate the transport of contaminants from the solution to the surface of Fe⁰-materials. However, in contrast to inert materials such as activated carbon [58-60], Fe⁰ dissolves in aqueous solutions [e.g. 29, 30, 61] and the dissolution is increased by any mixing procedure

[57, 62], yielding to more corrosion products. Indeed, mixing affects both the corrosion rate of the bare Fe^0 surface and the precipitation rate of iron oxides (or hydroxides). Prior to any film formation, high mixing rates lead to increased corrosion rates as the transport of cathodic species toward the Fe^0 surface is enhanced by turbulent transport. At the same time, the transport of Fe^{2+} ions away from the Fe^0 surface is also increased, leading to a lower concentration of Fe^{2+} ions at the Fe^0 surface. This results in a lower surface supersaturation and slower precipitation rate. Both effects contribute to less protective films being formed at high mixing rates [63]. This fundamental aspect has been acknowledged but not properly addressed in previous publications investigating the effects of mixing type and speed on Fe^0 reactivity. In fact, designed experiments [e.g. 64-66] did not include any non-mixed system (e.g. stirring with 0 rpm). On the other hand, mixing may be disadvantageous because in nature (and in column experiments) formed corrosion products remain mostly on the Fe^0 surface and limit the surface accessibility for contaminants [35, 67-70]. It is the objective of this study to discuss the effect of the film of corrosion products on the accessibility of the Fe^0 surface. For this purpose, the Fe^0 - H_2O system will be first presented.

THE Fe^0 - H_2O SYSTEM

Under natural conditions, the Fe^0 - H_2O system is a complex aggregate of elemental iron (Fe^0), water (H_2O), aqueous $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ species, various types of solid iron corrosion products (e.g. Fe_3O_4 , Fe_2O_3 , FeOOH) and dissolved gas (CH_4 , CO_2 , H_2 , H_2S , O_2). Thereby, water (H_2O) stands for the electrolyte. That is the solvent and the solutes (major ions, organic and inorganic contaminants). For the further presentation all solutes other than dissolved O_2 and contaminants will not be

addressed. For clarity, the $\text{Fe}^0\text{-H}_2\text{O}$ system will be first presented without contaminant and the contaminant behaviour in the system will be discussed.

In the $\text{Fe}^0\text{-H}_2\text{O}$ system, iron (Fe) exists in three different oxidation states (0, II, and III) and soluble species (Fe^{II} and Fe^{III}) may be available in a variety of aqua- and hydroxyl complexes [e.g., $\text{Fe}(\text{OH})_n^{n-2}$, $\text{Fe}(\text{OH})_n^{n-3}$, $\text{Fe}(\text{H}_2\text{O})_x^{2+}$, $\text{Fe}(\text{H}_2\text{O})_x^{3+}$ with $n \leq 3$ and $x \leq 6$]. In using elemental metals (Al^0 , Fe^0 , Cu^0 , Zn^0 and bimetallics) for groundwater remediation, a central aspect of the decontamination is that the electrochemical reduction reactions are mediated by the metal surface [19, 20, 53, 71-76]. In other words, in the case of elemental iron, contaminant molecules must be adsorbed at the surface or within conductive oxide films. Alternatively, contaminant molecules must first move onto the iron surface. The implication of this premise is that the contaminant transformation depends on the availability/accessibility of the Fe^0 surface and the electronic properties of the oxide-film. But the system contains several non-conductive solid phases (Fe_2O_3 and FeOOH) that will inhibit electron transfer and will inevitably compete with the Fe^0 surface for adsorptive contaminant removal. Furthermore, as shown below, from a pure thermodynamic perspective, the iron surface (Fe^0) is not necessarily the most powerful reductant. Therefore, contaminant adsorption/co-precipitation should be considered as an independent removal mechanism in $\text{Fe}^0\text{-H}_2\text{O}$ systems [41].

Redox systems in a $\text{Fe}^0\text{-H}_2\text{O}$ system

The redox reactivity of a $\text{Fe}^0\text{-H}_2\text{O}$ system is believed to primarily depend on the chemical thermodynamics of the two redox-systems of iron: $\text{Fe}^{\text{II}}/\text{Fe}^0$ ($E^0 = -0.44$ V) and $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ ($E^0 = 0.77$ V). Therefore, the aim of using Fe^0 -materials in remediating groundwater under anoxic conditions has been to exploit the negative potential of the couple $\text{Fe}^{\text{II}}/\text{Fe}^0$ to degrade or immobilize several redox-labile compounds [13, 17, 19, 20]. However, ferrous iron from the

$\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ redox couple, either in aqueous solution or adsorbed on mineral surfaces, can act as reductant for organic and inorganic soil components (e.g. MnO_2) [77-79] and contaminants [80, 81]. Furthermore, it has been shown that adsorbed or structural Fe^{II} (structural $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$: $E^0 = -0.34$ to -0.65 V) can be more powerful in reducing contaminant than the surface of Fe^0 (Fe^0 , $E^0 = -0.44$ V). On the other side recent results from Strathmann and co-workers [82] demonstrated that, when complexed with organic substances aqueous Fe^{II} (dissolved organic $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$: $0.520 \geq E^0(\text{V}) \geq -0.509$) are significantly more powerful than aqueous Fe^{II} ($E^0 = 0.77$ V). Therefore, abiotic contaminant reduction in a $\text{Fe}^0\text{-H}_2\text{O}$ system does not necessarily be mediated by electrons from the bulk metal. For example, chromium (VI) ($\text{Cr}^{\text{VI}}/\text{Cr}^{\text{III}}$; $E^0 = 1.51$ V) can be reduced by Fe^0 and all forms of Fe^{II} , whereas nitrate ($\text{N}^{\text{V}}/\text{N}^0$, $E^0 = 0.75$ V) can only be reduced by Fe^0 , structural Fe^{II} and dissolved organic Fe^{II} (see table 1). Thus, both nitrate and chromium can be reduced by electrons from Fe^0 (direct reduction) at the Fe^0 surface or in the matrix of corrosion products. Additionally, Fe^0 is not necessarily the most powerful reductant in a $\text{Fe}^0\text{-H}_2\text{O}$ system (E^0 values, Tab. 1). Before discussing the accessibility of the Fe^0 surface the possible reaction mechanisms will be discussed in the next section.

Possible contaminant removal mechanisms in a $\text{Fe}^0\text{-H}_2\text{O}$ system

Table 2 summarizes possible reaction pathways involved in the process of contaminant removal from the aqueous phase in a $\text{Fe}^0\text{-H}_2\text{O}$ system. Thereafter, contaminant removal can occur through four different mechanisms: precipitation, adsorption, co-precipitation, and reduction. Precipitation, adsorption, and co-precipitation are usually used to remove heavy metals from wastewater streams in adsorbing colloid flotation techniques. These three processes are also

important controlling phenomena dictating the concentration of metal ions in the environment [83].

The distinction between precipitation, co-precipitation, and adsorption is not always clear. Increasing the pH of a solution of a heavy metal ion will eventually result in the formation of an insoluble metal hydroxide precipitate (Eq. i, Tab. 2). Adsorption processes can occur whenever a solid substrate surface is present (Eq. ii, Tab. 2). For co-precipitation (Eq. iii, Tab. 2) to occur, a colloid must be preformed in the presence of the heavy metal ions (or generally the species) to be removed from solution. Metal ions are then adsorbed to colloids and entrapped in their structure while ageing [83-85].

In a $\text{Fe}^0\text{-H}_2\text{O}$ system at neutral pH, iron supersaturation in the vicinity of the Fe^0 surface yields to precipitation of amorphous and crystalline iron oxyhydroxides (Fe_3O_4 , Fe_2O_3 , FeOOH , $\text{Fe}(\text{OH})_2$, $\text{Fe}(\text{OH})_3\dots$) which are well-known for their adsorptive properties for organic and inorganic compounds [86, 87 and references therein]. Iron oxide precipitation is a dynamic process [88]: Therefore, some inflowing contaminants will be adsorbed onto aged iron oxyhydroxides (adsorption), others will be adsorbed onto nascent iron oxyhydroxides and will be entrapped in their structure while aging (co-precipitation). Finally, local supersaturation of the inflowing water can yield the contaminant precipitation (at the Fe^0 surface, within the porous oxyhydroxide matrix, or in the free pore volume). Contaminant precipitation is not likely to occur quantitatively in groundwater but may occur in a reactive barrier as the permeability decreases [89]. Beside the three discussed removal processes contaminant reduction by one of the available redox couples is possible (Eq. iv – vii, Tab. 2). For the reduction to occur at the Fe^0 surface, the contaminant must be transported to the surface (migration). Before discussing contaminant migration in the oxide-film, the nature of the film will be first discussed.

Nature of the oxide-film

Oxide-film formation is intrinsic to iron corrosion [27, 45, 46, 90, 91], and its development begins when Fe^0 -materials come in contact with water (Fig. 1a). As the film develops, a porous structure similar to a sponge is created in which soluble species (Fe^{II} - and Fe^{III} -species, H^+ , H_2 , O_2) are adsorbed (percolated) and/or become trapped (co-precipitation). The voids are usually filled with water (pore water). Because the process of oxyhydroxides ageing is usually accompanied by dehydration and conversion to a less porous structures [92, 93], it can be considered that oxide-film is multilayered and that the density increases from the outer surface of the film towards the metal (Tab. 3, Fig. 1). The porosity of the layers (and thus the specific surface area) decreases with increasing density, since the porosity and density are inversely proportional [32, 63]. Therefore, oxide-films are of microscopically heterogeneous structures [90, 91, 93, 96, 97]. In analogy to atmospheric corrosion, the porous oxide-film can be considered to consist of a film of mixed oxides in the cubic structure series (Tab. 3): FeO – Fe_3O_4 – Fe_2O_3 (ref. [96] and references therein). Thereby the outer layer of Fe_2O_3 can be replaced by the more hydrated non cubic FeOOH (Fig. 1b, Tab. 3).

CONTAMINANT MIGRATION TO THE Fe^0 SURFACE

Transport path and driving forces

In an undisturbed Fe^0 – H_2O system, the contaminant transport domain stretches from bulk of the solution through a porous surface film and ends at the Fe^0 surface (Fig. 1a). Table 1 shows clearly that certain dissolved species will be produced in the solution at the metal surface (e.g., Fe^{2+}) while others will be depleted (e.g., contaminant, H^+ , O_2). The established concentration gradients

will lead to molecular diffusion of the species (across the oxide-film) toward and away from the surface. On the other hand, the rate of the electrochemical processes depends on the species concentrations at the surface. Therefore, there is a two-way coupling between the electrochemical processes at the Fe^0 surface and processes in the adjacent solution layer (i.e., diffusion in the oxide-film).

Under common groundwater situations, the aqueous solution moves with respect to the Fe^0 surface. Therefore, the effect of convection on transport processes cannot be ignored. However, near-solid surfaces, in the oxide-film, time-averaged convection is parallel to the surface and does not contribute to the transport of species to and from the surface. In all the cases, very close to the surface no turbulence can survive and the species are transported solely by molecular diffusion (Fig. 2) and electromigration [33, 98]. Electromigration in the oxide-film depends essentially on the effective conductivity of the film composition (various iron oxides; E_{BG} in table 3) which in turn depend on three main factors [97]: the cross-sectional area available for conduction (porosity), the conductivity of the pore water, and the complexity of the pore space (i.e. tortuosity or pore size distribution). Shortly, the oxide-film may act as both ionic and electronic conductor.

Solutes migration across the oxide-film

Ideally, soluble species (Fe^{II} , Fe^{III} -species, H^+ , H_2 , O_2 , $\text{CO}_2/\text{HCO}_3^-$, contaminants) migrate freely across the film to the Fe^0 surface. This ideal case is, however, unlikely because almost all soluble species (contaminants in particular) interact more or less strongly with the oxide-film and the pore structure is complex (tortuosity). From the above presentation, it is obvious that the transport of a contaminant from the bulk solution to the surface of Fe^0 -materials (et vice versa the transport of reaction products in the opposite direction) will occur in a double layer flow field

(Fig. 2): (i) turbulent in the bulk solution yielding to rapid solutes/contaminants accumulation at the outer surface of the oxide-film and (ii) diffusive across the porous oxide-film to the Fe^0 surface. So, the transport of species in the bulk is dominated by turbulent mixing, while in the oxide-film closer to the surface is controlled by molecular diffusion. In both flow fields, provide that the species are electrical charged, electromigration plays a role but it can be emphasised that the role of electromigration is more significant in the oxide-film. These transport processes can only be observed if the $\text{Fe}^0\text{-H}_2\text{O}$ system remains undisturbed [33, 41, 99]. In this regard, because of the disturbance of oxide-film formation, mixing can be considered as the major disturbing factor for hitherto mechanistic investigations with Fe^0 - materials [56, 94].

Generally, in such a transport process, if molecular diffusion is much faster than the electrochemical reactions, contaminant concentration change at the Fe^0 surface will be small. If on contrary the diffusion is slower than electrochemical reactions, contaminant concentration of species at the Fe^0 surface (in the pore water) can become very different from the ones in the bulk solution respectively at the outer surface of the oxide-film. The next section will discuss the contaminant migration across the oxide-film.

Contaminant migration across the oxide-film

Mass transfer within an oxide-film relies on the physical structure of the film (thickness, porosity/density, morphology), the properties of the contaminant (size, electrical charge, affinity for film material) and the fluid dynamic regime [100]. As discussed above, contaminant migration across the oxide-film is governed by molecular diffusion and electromigration. The molecular diffusion is aroused through the concentration gradients between the groundwater and the pore water and the charge of the contaminant (electromigration). Since the driving force for

contaminant reduction (electromotive force, e.m.f) in a given $\text{Fe}^0\text{-H}_2\text{O}$ system is the same for all species (contaminants and other solutes), the migration across the film will primarily depends on film permeability. That is on the pore structure and the pore size distribution (tortuosity). Therefore, for a contaminant to migrate across an oxide-film, its should be of sufficient small size. Similarly, the reaction products (primarily Fe^{2+} and H_2) will be transported across the oxide-film to the groundwater. However, contaminants can be accumulated at the outer surface of the oxide-film. Furthermore, once inside the oxide-film, inflowing contaminants may adsorb to its surface, and eventually co-precipitate with newly formed iron oxide. Therefore, due to diffusion limitations, there will be a finite depth to which contaminants can penetrate before been directly reduced by electrons from Fe^0 or indirectly reduced by structural Fe^{II} (or eventually by organic Fe^{II}). Note that if organic Fe^{II} is present, contaminant reduction can even occur in the aqueous solution.

When further consider the fact that all solid corrosion products are of larger surface area than the Fe^0 surface (Tab. 3), compete with the Fe^0 surface for contaminant removal and that the Fe^0 surface is (at least partly) shielded by these corrosion products (Fig. 1), it become clear that quantitative contaminant reduction at the Fe^0 surface is not likely to occur. For an oxide-adsorbed contaminant to further migrate to the Fe^0 surface, a driving force must exist that overcome strong columbic interactions, such a driving force has not been reported in the reactive wall literature. Therefore, the central premise, that quantitative contaminant removal occurs through electrons from the bulk Fe^0 -materials is only realistic if the oxide-film is electronic conductive. Such a film has not been reported from field barriers ([10] and references therein).

DISCUSSION

The primary step in the aqueous Fe^0 oxidation (iron corrosion) at pH values > 4.5 is the formation of a multi-layered oxide-film at the Fe^0 surface [90, 91]. Under most circumstances, these layers are thick, porous and therefore non-protective [27-30]. This non-protective property of the oxide-film is the essential characteristic making elemental iron (Fe^0 -materials) appropriate for groundwater remediation [45, 46, 101]. The basic concept is to utilize contaminants as electron acceptors for progressive Fe^0 dissolution. Ideally, Fe^0 -materials should oxidize only from the electron transfer to a contaminant. Unfortunately, water (H_2O) has the ability to oxidize Fe^0 -materials both by a chemical and an electrochemical mechanism ([49] and references therein). Fe^0 -materials oxidation by water yields an oxide-film at the material surface at an earlier time scale of the reactive wall life before any quantitative contaminant inflow occurs [25, 27, 102]. Therefore, for a contaminant to reach the Fe^0 surface it has to migrate across an oxide-film. In the same manner, Fe^{2+} ions from iron corrosion must migrate across the oxide-film to come in the bulk groundwater. Since the oxide-film is a good adsorbent for both contaminant and Fe^{2+} ions (resulting in more reactive structural Fe^{II}), contaminant reduction may occur at the meeting point within the oxide-film. When considering diffusion processes within the oxide-film it can be concluded on the basis of size exclusion phenomena that the meeting point for contaminant and Fe^{2+} ions will be more or less far from the Fe^0 surface. In fact, Fe^{2+} ions migrate in the direction of increasing pore sizes and contaminants in the opposite direction. In all the cases quantitative contaminant reduction at the surface of Fe^0 is not likely to occur and direct reduction within the oxide-film is also not likely since the film is not necessarily electronic conductive.

In order to obtain the parameters for the design of reactive walls and to determine the optimum size and operating conditions, mathematical models describing the removal process have been developed [103, 104]. Available models assume a contaminant reduction at the Fe^0 surface. The present study has shown that this assumption is not acceptable. Contaminant removal primarily

occurs through adsorption/co-precipitation onto/with corrosion products. The further eventual abiotic contaminant reduction depends on the availability of secondary reductants (Fe^{II} , H^+/H_2), the porosity and the tortuosity of the oxide-film, and the conductivity of oxide-film. If the oxide-film is mostly made of conductive Fe_3O_4 , electron from the Fe^0 surface can be transfer to the contaminant which can be reduced within the oxide-film or at the interface oxide/ H_2O [37, 94]. Therefore, Fe^0 acts both as source of corrosion products for contaminant adsorption and as a generator of Fe^{II} and H_2 for possible catalytic contaminant reduction. Beside these abiotic mechanisms, contaminants can be reduced at the site of their adsorption (more or less far from the metal surface) by indigenous micro organisms [105].

A convincing argument for contaminant sorption/co-precipitation onto/with corrosion products (oxide-film) as initial removal mechanism is the manifold observed lag time between the date of Fe^0 -materials addition and the begin of quantitative contaminant removal [55, 106-108]. Elusive arguments have been proposed to rationalise this experimental evidence. However, from the above discussion and recent experimental works from Noubactep and co-workers [55, 56, 107], it is evident that the lag time is the time for sufficient corrosion products to be generated (41). For example, in a non disturbed “ $\text{Fe}^0\text{-H}_2\text{O-FeS}_2\text{-U(VI)}$ ” system at pH 4.0 – 4.5, this lag time could lengthen to 40 days [107].

For the further development of the Fe^0 walls technology it is urgent to characterise the effects of major ions and environmental ligands on the porosity and the adsorption capacity of several contaminant by $\text{Fe}^0\text{-H}_2\text{O}$ systems. Background knowledge in this area is widely available in the literature [86, 109–111]. For example, Garman et al. [109] investigated the kinetics of chromate adsorption on goethite in the presence of adsorbed silicic acid over a range of pH values and silicic acid concentrations common in natural systems. By repeating such an experiment under non mixing conditions while replacing goethite by well-characterised Fe^0 -materials, reliable

qualitative information can be gained over the processes of Cr(VI) removal in different Fe⁰-H₂O systems.

CONCLUSIONS

The objective of this literature review was to establish that the development of an oxide-film is a characteristic of aqueous iron corrosion. This film controls the rate of mass transfer of contaminant between the water phase and the Fe⁰ surface. Since the film growth is a dynamic process [88], contaminants may co-precipitate with iron oxides/hydroxides. Therefore, beside adsorption onto solid surfaces and co-precipitation with colloidal iron oxides/hydroxides, contaminant reduction is the other possible removal mechanism for each contaminant. Therefore adsorption and co-precipitation should be considered as independent removal mechanism.

Since oxide-film are initially porous, reduction can occur either at the Fe⁰ surface or within the oxide-film. However, contaminant transport across the oxide-film is limited by diffusion and contaminant reduction within the film may be thermodynamically more favourable than at the Fe⁰ surface. Therefore, it is not likely that quantitative contaminant reduction occurs at the Fe⁰ surface or/and through electrons from the bulk metal. This evidence was overseen for a decade because mechanistic investigations were mostly conducted under mixing (shaking, stirring) conditions. Results from experiments under mixing conditions may be reproduced. However, under these conditions, iron corrosion is accelerated, oxide-film formation at Fe⁰ surface is avoided or delayed, corrosion products nucleation and precipitation in the bulk solution is accelerated.

For the further development of reactive walls it is urgent to investigate factors which may sustain the porosity of the oxide-film. In fact, the oxide-film porosity may significantly decreased as the

film growths or as result of biological activity. Thus, both the inflowing of contaminant and the out-flowing of secondary reductants (Fe^{II} , H_2 , H) may become too slow for satisfactorily remediation goal. Targeted experiments to properly address the findings of this study is a challenge for the scientific community.

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Table 1: Standard electrode potentials of all possible redox couple of iron relevant for Fe⁰ barriers, ubiquitous groundwater constituents (H⁺, O_{2(aq)}, MnO₂), and three selected contaminants (C₂Cl₄, NO₃⁻, CrO₄²⁻). Whenever possible, electrode potentials are arranged in increasing order of E⁰. An electrochemical reaction occurs between an oxidant of higher E⁰ and a reductant of lower E⁰. Therefore, under certain conditions (E⁰ < -0.44 V) structural and organic Fe^{II} are more powerful reductants than Fe⁰ (see text).

redox couple		E ⁰ (V)	Eq.
		(SHE)	
Fe ⁰	⇌ Fe ²⁺ + 2 e ⁻	- 0.44 ^a	(i)
Fe _(s) ²⁺	⇌ Fe _(s) ³⁺ + e ⁻	-0.34/-0.65 ^b	(ii)
Fe _{org} ²⁺	⇌ Fe _{org} ³⁺ + e ⁻	0.52/-0.51 ^c	(iii)
2 H ⁺ + 2 e ⁻	⇌ H ₂ (g)	0.00 ^a	(iv)
C ₂ Cl ₄ + H ⁺ + 2 e ⁻	⇌ C ₂ HCl ₃ + Cl ⁻	0.59	(v)
NO ₃ ⁻ + 6 H ⁺ + 5 e ⁻	⇌ ½ N ₂ (g) + 3 H ₂ O	0.75 ^a	(vi)
Fe ²⁺	⇌ Fe ³⁺ + e ⁻	0.77 ^a	(vii)
O ₂ + 2 H ₂ O + 4 e ⁻	⇌ 4 OH ⁻	0.81 ^a	(viii)
MnO ₂ + 4 H ⁺ + 2 e ⁻	⇌ Mn ²⁺ + 2 H ₂ O	1.23 ^a	(ix)
CrO ₄ ²⁻ + 8 H ⁺ + 3 e ⁻	⇌ Cr ³⁺ + 4 H ₂ O	1.51 ^a	(x)

^a ref. [50]; ^b ref. [23]; ^c ref. [82]

Table 2: Possible reaction pathways for contaminant (Ox) removal from the aqueous phase in a $\text{Fe}^0\text{-H}_2\text{O}$ system and their reversibility under natural conditions. Reaction xiv depicts the direct reduction that is currently considered as the major reaction path (Fe^0 Reduction). Since the iron surface is always covered with an oxide-film, Fe^0 Reduction can only occur if the film is electronic conductive (see text).

Mechanism	Reaction	Reversibility	Eq.
Precipitation:	$\text{Ox}_{(\text{aq})} + n \text{OH}^- \Leftrightarrow \text{Ox}(\text{HO})_{n(\text{s})}$	Reversible	(xi)
Adsorption:	$\text{S}_{(\text{sorption site})} + \text{Ox} \Leftrightarrow \text{S-Ox}$	Reversible	(xii)
Co-precipitation:	$\text{Ox} + n \text{Fe}_x(\text{OH})_y^{(3x-y)} \Leftrightarrow \text{Ox}-[\text{Fe}_x(\text{OH})_y^{(3x-y)}]_n$	Irreversible	(xiii)
Fe^0 Reduction:	$\text{Fe}^0 + \text{Ox}_{(\text{aq})} \Rightarrow \text{Red}_{(\text{s})} + \text{Fe}^{2+}$	Irreversible	(xiv)
$\text{Fe}^{2+}_{(\text{aq})}$ Reduction:	$\text{Fe}^{2+}_{(\text{aq})} + \text{Ox}_{(\text{aq})} \Rightarrow \text{Red}_{(\text{s})} + \text{Fe}^{3+}_{(\text{aq})}$	Irreversible	(xv)
$\text{Fe}^{2+}_{(\text{s})}$ Reduction:	$\text{Fe}^{2+}_{(\text{s})} + \text{Ox}_{(\text{aq})} \Rightarrow \text{Red}_{(\text{s})} + \text{Fe}^{3+}_{(\text{s})}$	Irreversible	(xvi)
$\text{Fe}^{2+}_{(\text{org})}$ Reduction:	$\text{Fe}^{2+}_{(\text{org})} + \text{Ox}_{(\text{aq})} \Rightarrow \text{Red}_{(\text{s})} + \text{Fe}^{3+}_{(\text{org})}$	Irreversible	(xvii)

Table 3. Some properties of iron and selected iron oxides likely to be present in a Fe⁰-H₂O system. E_{BG} = energy necessary to excite an electron from the valence band to the conduction band (from ref. [94]) and surface area of oxides compiled by Cornell and Schwertmann [87]. Density values are from ref. [95].

Substance	Formula	Structure	E_{BG} (eV)	Density (g/cm ³)	Fe/O	Surface (m ² /g)
Iron	Fe	bcc	–	7.86	–	< 2
Wüstite	FeO	cubic		5.67	3.50	
Magnetite	Fe ₃ O ₄	cubic	0.11	5.18	2.63	4–100
Maghemite	Fe ₂ O ₃	cubic	2.03	4.69	2.33	
Goethite	α-FeOOH	orthorhombic	2.10	4.28	1.75	
Lepidocrocite	γ-FeOOH	orthorhombic	2.06	4.09	1.75	15–260
Feroxyhyte	δ-FeOOH	hexagonal	1.94		1.75	

Figure 1

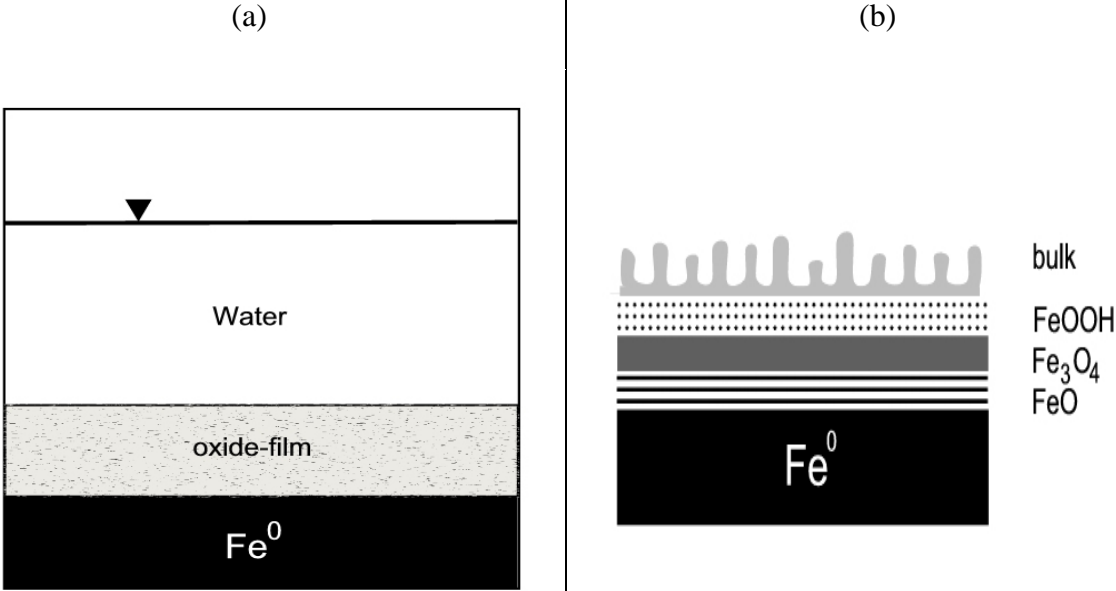
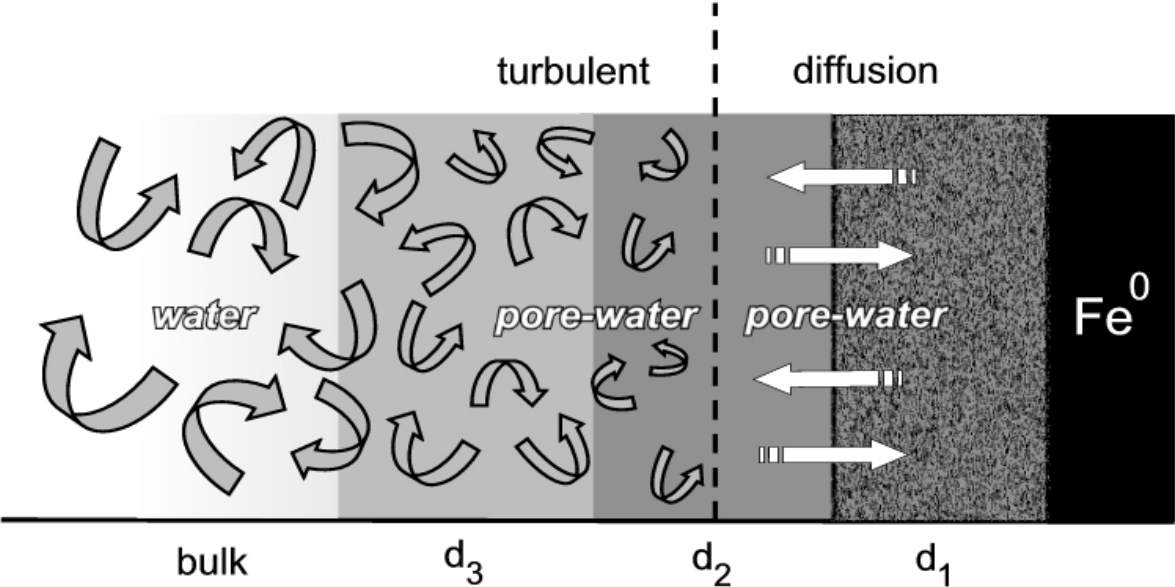


Figure 2:



FIGURES CAPTIONS

Figure 1: (a) Sketch of the transport pathway of a contaminant from the bulk solution to the surface of Fe^0 .

(b) Possible structure of the porous film in analogy to atmospheric corrosion. The Fe_2O_3 -layer (see text) is substituted by the hydrated FeOOH -layer.

Figure 2: Sketch of the double layer flow field of solute (e.g. contaminant) transport from the bulk solution to the surface of Fe^0 (after Nordsveen et al. [33]): d_1 is the porous film; d_2 is the diffusion sublayer and d_3 is the turbulent sublayer. It is assumed that the turbulent field ends in the middle of d_2 . Quite different transport rates are typically found in individual regions: large in the turbulent boundary layer (bulk and d_3), intermediate in the molecular diffusion-dominated boundary layer (d_2), and low in the porous film (d_1).