

Contaminant reduction at the surface of elemental iron: the end of a myth

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Der Einsatz von metallischem Eisen (Fe^0) in der Wasseraufbereitung beruht darauf, dass die Reduktion mehrerer Schadstoffe mit der Eisenkorrosion gekoppelt werden kann. Diese thermodynamisch fundierte Annahme wurde von den Pionieren der Reaktionswandtechnologie vorgeschlagen und von der Fachwelt angenommen. Doch es ist seit Jahrzehnten dokumentiert, dass die Eisenkorrosion zwangsläufig zu einer Oxiddeckschicht führt, welche beispielsweise die Diffusion von Sauerstoff (O_2) erschweren bzw. auf Dauer verhindern kann. Da die meisten in Frage kommenden Schadstoffe größer als O_2 sind, ist eine quantitative Schadstoffreduktion an der Eisenoberfläche unwahrscheinlich. Auf Grundlage einer Literaturstudie und eigenen Untersuchungen ist zu schlussfolgern, dass eine quantitative Schadstoffreduktion in einer Eisenreaktionswand primär katalytisch durch Fe^{II} -Spezies in der Oxiddeckschicht erfolgt. Dabei dient metallisches Eisen als Eisenoxidproduzent für die Schadstoffadsorption und als Fe^{II} -Generator für eine eventuelle Schadstoffreduktion.

The rationale for using elemental iron (zerovalent iron, ZVI) to treat contaminated waters is based on the fact that many contaminants can be reduced when coupled to the oxidation of iron (iron corrosion). This thermodynamically supported hypothesis has been introduced by the pioneers of the permeable barrier technology and is largely accepted by the scientific community. However, it has been established that iron corrosion inevitably yields an oxide film at the metal surface which acts as a diffusion barrier for a specie as small as molecular oxygen (O_2). Therefore, quantitative contaminant reduction at the surface of ZVI is physically not likely. 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 ZVI, it takes place within the mass of corrosion products and not at the surface of ZVI. It is concluded that ZVI acts both as source of corrosion products for contaminant adsorption and as a generator of Fe^{II} for possible catalytic contaminant reduction.

1 Introduction

Groundwater contamination is one of the most difficult and expensive environmental problems (MCMURTY & ELTON 1985). The most common technology used to remediate groundwater is the pump-and-treat technology (pump the water and treat it at the surface). Because of recognized limitations of pump-and-treat technologies (MACKAY & CHERRY 1989), alternative innovative solutions are currently under development, in-situ permeable reactive barrier technology been one of the most promising innovative solutions. Reactive permeable barriers (reactive walls) are discussed as economically preferable alternatives (GILLHAM & O'HANNESIN 1994; STARR & CHERRY 1994). Yet operating reactive walls treat contaminations like halogenated hydrocarbons, chromium, nitrate, and radionuclides (EBERT 2004; PULS *et al.* 1999; SCHERER *et al.* 2000; TRATNYEK *et al.* 2003; WARNER & SOREL 2003; WILKIN *et al.* 2003).

Zerovalent iron (ZVI) as reactive medium for reactive walls is the most tested and promising material because metallic iron is readily available and of low-cost. In addition, iron waste particles from industrial filings can be used as barrier material (LEE *et al.* 2003; NOUBACTEP *et al.* 2005). Reactive walls containing metallic iron are currently being developed for in situ treatment technology (BIGG & JUDD 2001; EBERT 2004; TRATNYEK *et al.* 2003; WARNER & SOREL 2003; WILKIN *et al.* 2003). As a strong reducer, zerovalent iron has been used to remove several organic and inorganic contaminants. Whereas the decontamination effect in the presence of ZVI is sure, reported results on removal mechanisms for several contaminants are not univocal (e.g. MANTHA *et al.* 2001; NOUBACTEP *et al.* 2006a; SCOTT *et al.* 2005).

The removal of any contaminant through a direct reaction at the surface of ZVI (heterogeneous reaction) requires that the reactant molecules

reach the solid surface. However, this surface is known to be the site of production of hydrated oxides of iron (corrosion products) which strongly interact with several contaminants, possibly avoiding quantitative ZVI surface accessibility for many contaminants of interest. On the other hand corrosion products are adsorption sites for Fe^{II} ions from continuously corroding iron. The role of surface bound Fe^{II} for contaminant reduction has been studied (BEHRENDTS & VAN CAPPELLEN 2005; HANSEN *et al.* 1994; JOHNSON *et al.* 1998; WHITE & PATERSON 1996), and it was found that Fe^{II} adsorbed on mineral surfaces plays an important role in the process of contaminant reduction.

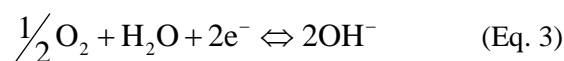
At this stage it is evident that contaminant removal in a “ZVI–H₂O”–system may be either the result of (i) direct reduction at the surface of ZVI, (ii) catalytic reduction through Fe^{II} at the surface of corrosion products or (iii) adsorption onto corrosion products. Furthermore, when precipitating corrosion products may entrap adsorbed contaminants in their mass; this retention mechanism is known as coprecipitation (CRAWFORD *et al.* 1993; SRIDHARAN & LEE 1972). Therefore, contaminants are removed from the aqueous phase through three different mechanisms (adsorption, coprecipitation and reduction) and spatially at three different possible sites (at the surface of ZVI, within the film of corrosion products and at the surface of corrosion products).

The objective of this study is to theoretically discuss both the most probable reaction mechanism and the most probable reaction site. For this purpose the process of iron corrosion will be first presented.

2 The process of aqueous iron corrosion

A voluminous literature exists on the corrosion of iron and steel, which are currently used as ZVI materials. 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 rust 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 (oxygen) diffusion as will be shown below.

Aqueous iron corrosion occurs by two different mechanisms: chemical and electrochemical oxidation. Even though aqueous chemical iron oxidation (DRAZIC & POPIC 2005; EVANS 1945; GERASIMOV *et al.* 1985; KLAS & STEINRATH 1975) can not be excluded, immersed iron corrosion (e.g. in reactive walls) is generally agreed to occur through an electrochemical mechanism (DE LA RIVE 1830; MATHESON & TRATNYEK 1994; POWELL *et al.* 1995; SNOEYINK & JENKINS 1980; VERNON 1945; WEBER 1996; WHITMAN *et al.* 1924; WILSON 1923). A consideration of the simple voltaic cell helps materially to clarify one’s ideas in this connexion. The essential features to observe are (i) the electrolyte (e.g. 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 positively charged metal ions (Fe²⁺) 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, immersed iron corrosion can be regarded as to be made up of anodic and cathodic components. The anodic process is the iron dissolution (Eq. 1). Depending on the cathodic process, two main types of aqueous iron corrosion have been described: (i) hydrogen evolution type (Eq. 2) and (ii) oxygen absorption type (Eq. 3).



2.1 Hydrogen evolution corrosion

The characteristic feature of “hydrogen evolution corrosion” is the liberation of hydrogen as hydrogen gas (H₂) 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 (Evans 1945). Therefore, the rate at which fresh acid 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 (Vernon 1945). Since natural waters are generally of near neutral pH, corrosion with oxygen absorption is more interesting for the discussion in this paper.

2.2 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. 3). 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 (HUANG & ZHANG 2005; STRATMANN & MÜLLER 1994). Therefore, in the vast majority of cases the rate of iron corrosion predicted by the available oxygen is considerably less than the theoretical rate that is possible when the requisite amount of oxygen is forthcoming (VERNON 1945).

2.3 Implications for ZVI reactive walls

The main conclusion from this literature survey is that iron corrosion at neutral pH values 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 ZVI materials in the groundwater remediation. In fact, while using ZVI materials in the subsurface remediation (mostly under

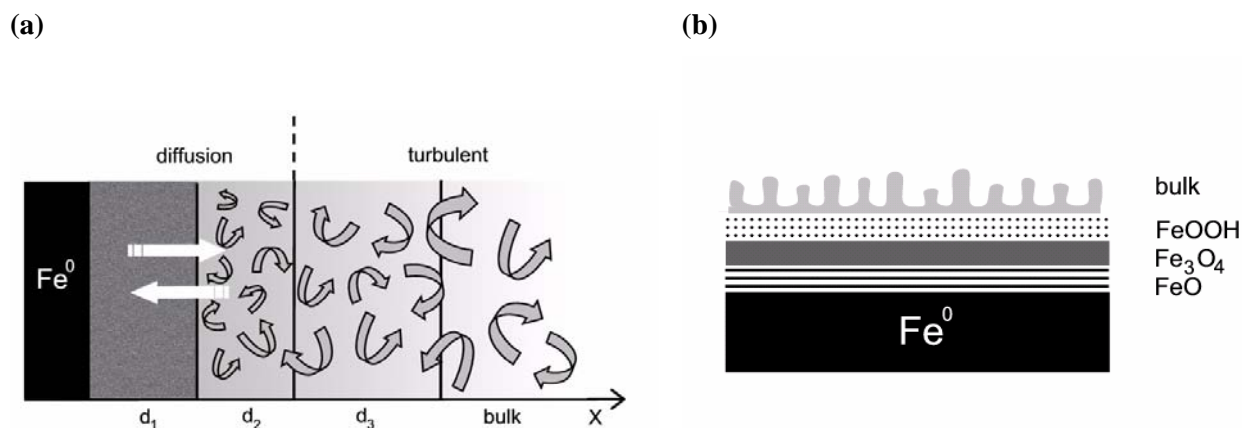


Fig. 1: (a) Sketch of the transport pathway of a contaminant from the bulk solution to the surface of Fe^0 (after NORDSVEEN *et al.* 2003): d_1 is the porous film; d_2 is the diffusion sublayer and d_3 is the turbulent sublayer. d_1 and d_2 compose the surface film thickness and d_3 is the liquid boundary layer thickness.

(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.

nearly anoxic conditions), it is assumed that electro-active contaminants will sustain iron corrosion in the same way as molecular oxygen as discussed above. However, any contaminant of interest must come through 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 a “ZVI–H₂O”-system. The next section discusses the contaminant transport to the metal surface.

3 Contaminant transport to the surface of ZVI

As with all solid–liquid heterogeneous reactions, the reduction process should take place by transfer of contaminants from bulk solution to the iron metal surface followed by chemical reaction (electron transfer) at the ZVI surface. The overall process has been shown to be mass transfer-limited (e.g. NAM & TRATNYEK 2000). In the absence of oxygen the electromotive force (e.m.f.) of the overall reaction is believed to provide the driving force for the reductive decontamination reaction coupled with the oxidation of the iron. The plausibility of this chemical component of the remediation process is addressed in this section while focussing the interest on the surface accessibility for the contaminant. For this purpose the transport path must be described.

3.1 Pathway and mechanism of contaminant transport

In an undisturbed “ZVI–H₂O”-system, the contaminant transport domain stretches from bulk of the solution through a porous surface film and the mass-transfer boundary layer and ends at the ZVI surface, as sketched in Figure 1a. In analogy to atmospheric corrosion, the porous film can be considered to consist of a film of mixed oxides in the cubic structure series: FeO–Fe₃O₄–Fe₂O₃ (Figure 1b) (ALLEN *et al.* 1974; SCOTT *et al.* 2005; NOUBACTEP *et al.* 2006b). In all cases, it is obvious that the transport of a contaminant from the bulk solution to the surface of ZVI where quantitative reduction is supposed to occur may be limited by diffusion processes. Simplifying, Figure 1a shows that a double layer flow field can be assumed: (i) turbulent in the bulk solution and (ii) diffusive in the diffusion sublayer and the porous film. So, the transport of species in the bulk is dominated by turbulent mixing, while

in the sublayer closer to the surface and in the porous surface film it is controlled by molecular transport (diffusion). These transport processes can only be observed if the system remains undisturbed (NORDSVEEN *et al.* 2003; NOUBACTEP *et al.* 2006b). In this regard, mixing is considered as a disturbing factor for mechanistic investigations with ZVI materials (NOUBACTEP *et al.* 2006a, 2006b). In fact, increasing mixing rate accelerates aqueous iron corrosion, yielding more corrosion products which compete with the surface of iron for contaminant adsorption. Indeed, mixing affects both the corrosion rate of the bare ZVI 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 ZVI surface is enhanced by turbulent transport. At the same time, the transport of Fe²⁺ ions away from the ZVI surface is also increased, leading to a lower concentration of Fe²⁺ ions at the ZVI 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 (NESIC & LEE 2003).

3.2 Process of contaminant transport to the surface of ZVI

First of all it should be pointed out that the mass transfer-limitation of the decontamination process as described in the reactive wall literature (e.g. increasing removal rate with increasing mixing rate – e.g. NAM & TRATNYEK 2000) primarily addresses the transport of the contaminant from the bulk solution to the vicinity of iron surface. As discussed above, quite different transport rates are typically found in individual regions (Figure 1a), large in the turbulent boundary layer, intermediate in the molecular diffusion-dominated boundary layer, and low in the porous film (NORDSVEEN *et al.* 2003).

Irrespective from the transport rate, a contaminant has to find its way through a tangled maze of pores in the oxide film (NESIC & LEE 2003) to reach the ZVI surface. However, contaminants are primarily adsorbed due to electrostatic attractions from adsorbing surfaces. In this regard the surface of ZVI material is doubly disadvantaged: (i) it is covered by the oxide-film (limited accessibility) and (ii) it has less (or no) functional groups. Therefore, there is no reason for on oxide film adsorbed contaminants to quantitatively migrate to the metal surface. Even though the

e.m.f. could be stronger than adsorptive forces, the migration of the species through the porous film (Figure 1b) to the ZVI surface may be very slow. On the other hand Fe^{II} ions produced at the ZVI surface diffuse more favorable in the opposite direction. Consequently, an adsorbed species can be (a) entrapped in the matrix of aging corrosion products (coprecipitation), (b) reduced by structural Fe^{II} or atomic/molecular hydrogen (H/H_2) from iron corrosion or (c) reduced by electrons from metallic iron if the oxide is conductive (ODZIEMKOWSKI *et al.* 1998). Note that even coprecipitated contaminants can be further reduced. In all cases the decontamination process did not occur at the surface of ZVI. This evidence has been mostly overseen due to mixing reaction vessels in experiments with ZVI material. This experimental tool is very helpful when accelerating contaminant transport to an inert surface as that of activated carbon but should be avoided when working with materials as elemental iron that interacts with water.

3.3 Discussion

Pollutant removal by ZVI primarily depends 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). Both the aqueous solution behavior and the redox thermodynamics are of interest. The primary aim of using ZVI in groundwater remediation 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 (GILLHAM & O'HANNESIN 1994; MATHESON & TRATNYEK 1994; POWELL *et al.* 1995; WEBER 1996). However, ferrous iron from the $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ redox couple, either in aqueous solution or adsorbed on mineral surfaces (structural Fe^{II}), can be part of a convenient delivery path for electrons, reducing and immobilizing organic and inorganic pollutants (NAKA *et al.* 2006; WHITE & PATERSON 1996). Furthermore, pollutant coprecipitation with corrosion products has been demonstrated as another removal pathway (CRAWFORD *et al.* 1993; SRIDHARAN & LEE 1972). Therefore, in a "ZVI- H_2O "-system, there are three possible immobilization pathways for several pollutants: (i) adsorption onto corrosion products or at the surface of ZVI; (ii) reduction by Fe^0 , Fe^{2+} or H_2 (H) and (iii) coprecipitation with corrosion products. The potential of structural $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ has been determined by WHITE & PATERSON (1996) to be comprised between -0.34 and -0.65 V (see also NAKA *et al.* 2006 for complexed iron species). This shows that struc-

tural Fe^{II} is stronger than aqueous Fe^{II} and can even be stronger than ZVI (Fe^0) for contaminant reduction. As shown above contaminants are first adsorbed onto (or coprecipitated with) iron corrosion products. For them to be reduced there are two possibilities: (i) structural Fe^{II} diffuses to their location within the oxide film (alternatively aqueous Fe^{II} diffuses and adsorbs in their vicinity) or (ii) electrons come from ZVI provided that the oxide film is conductive. 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.

4 Conclusions

Although the role of oxide-film in influencing species transport to the iron surface has been well-established in the corrosion literature for decades (LAVINE *et al.* 2001; STRATMANN & MÜLLER 1994; VERNON 1945; WILSON 1923; WHITMAN *et al.* 1924) it is only poorly reflected in investigations regarding the processes of contaminant removal in "ZVI- H_2O "-systems. While neglecting this key issue elusive arguments have been postulated unsupported by experimental evidence or supported by reproduced data from wrong experimental conditions (shaking or stirring). Some researchers (e.g. ODZIEMKOWSKI *et al.* 1998) have shown in column studies that, under anoxic conditions, the surface of ZVI is covered by a porous film of magnetite and that the further decontamination takes place at the porous film/solution interface, since magnetite is electron conducting. However, irrespective from the conductive properties of the oxide films, it has been recognised for decades that freshly precipitated iron oxides quickly scavenges heavy metals and organics (BROWN *et al.* 1999; SRIDHARAN & LEE 1972 and references therein). Therefore, contaminant adsorption onto corrosion products is the primary mechanism of contaminant removal from the aqueous phase. Adsorbed contaminant may precipitate with ageing corrosion products (coprecipitation) more or less far from the ZVI surface. Since corrosion products are porous dissolved Fe^{II} -species, atomic and molecular hydrogen (H and H_2) from corroding ZVI can diffuse to the oxide film and reduce contaminants within the film of corrosion products. Therefore, quantitative contaminant reduction at the surface of ZVI materials is a myth.

This myth has survived a decade mostly because mixing (shaking or stirring) laboratory vessels

yields reproducible results, but as discussed above, this operation accelerates iron corrosion, avoids or delays oxide film formation at ZVI surface, and accelerates corrosion product precipitation in the bulk solution. For the further development of reactive walls it is urgent to investigate factors which may sustain the porosity of the oxide film. With other words, at any specific site factors capable of enhancing or decreasing oxide film porosity have to be identified. To gain an overview on the general trends, long term laboratory investigations with common environmental species (e.g. major ions, environmental ligands) and well characterised ZVI materials can be conducted.

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