

Investigating Contaminant Removal in “Fe⁰-H₂O” Systems

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Der Einsatz von elementarem Eisen (Fe⁰ oder Fe⁰-Träger) in der Umweltsanierung ist ohne Zweifel eine der genialsten Ideen, die die Sanierungsfachwelt in den letzten Jahren fasziniert hat. Nach den ersten Erfolgsmeldungen beim Einsatz von Eisenreaktionswänden und der - obgleich umstrittenen - Einführung von Eisennanopartikeln u.a. zur Quellsanierung entstand der Eindruck, als wären Eisenmaterialien das Mittel der Wahl für alle Umweltsanierungsfälle. Eine nähere Betrachtung des Fe⁰-H₂O-Systems zeigt jedoch, dass Fe⁰-Träger unter Umweltbedingungen kein elementares Eisen (Fe⁰) zur Verfügung stellen können. Somit kommen Fe⁰-Träger als Reduktionsmittel, wie ursprünglich angenommen, nicht in Frage. Anhand einer Literaturstudie bekräftigt der vorliegende Beitrag die Nicht-Existenz einer Fe⁰/H₂O Grenzfläche und schlägt eine neue Vorgehensweise für die Untersuchung der in Fe⁰-H₂O-Systemen ablaufenden Prozesse vor. Demnach kann in Langzeitversuchen der Einfluss diverser Schadstoffe auf das Referenzsystem Fe⁰-H₂O untersucht werden. Dabei wird vor allem untersucht, welche hemmenden oder fördernden Einflüsse einzelne Schadstoffe auf die Eisenkorrosion unter umweltrelevanten Bedingungen ausüben.

The use of elemental iron materials (Fe⁰ or Fe⁰ carriers) in the environmental remediation is one of the ideas that have fascinated environmental scientists during the last two decades. After the successful implementation of first iron walls and the controversial use of iron nanoparticles for treatment of contaminant source zones, Fe⁰ materials seem to be the media of choice for all contamination events. A critical consideration of the Fe⁰-H₂O system reveals that Fe⁰ carriers can not deliver Fe⁰ (elemental iron) under environmental conditions. Therefore the premise of direct contaminant reduction at the surface of Fe⁰ materials is no more valid. The present study reiterates the non existence of a Fe⁰/H₂O interface and suggests a new approach for the investigation of processes in Fe⁰-H₂O systems. Thereafter, for a given Fe⁰ material, long-term undisturbed batch experiments should be performed for individual contaminants with the contaminant free Fe⁰-H₂O system as reference. The proposed approach can be regarded as the investigation of the inhibitory or promotional effects of individual contaminants on the process of iron corrosion under relevant environmental conditions.

1 Introduction

Elemental iron materials (iron-based alloys, Fe⁰ carriers or Fe⁰) have been used as an abiotic contaminant reducing reagent for organic and inorganic groundwater contaminants for over 12 years (ALONSO *et al.* 2002, BIGG & JUDD 2000, O'HANNESIN & GILLHAM 1998, SCHERER *et al.* 2000, TRATNYEK 1996). In this context, a Fe⁰ carrier is mostly cast iron and low-alloyed steel, and is widely termed as zerovalent iron; contaminants have been denoted as oxidants/reductates, and the bare surface of Fe⁰ materials as reductant. The reducing capacity of elemental iron is supposedly due to the low standard reduction potential of the redox couple Fe^{II}/Fe⁰ ($E^0 = -0.440$ V). This potentially makes Fe⁰ a reducing agent relative to several redox labile substances, including hydrogen ions (H⁺) and oxygen (O₂).

The exclusive consideration of the redox couple Fe^{II}/Fe⁰ has led to the premise, that quantitative contaminant reduction occurs at the surface of iron materials. However, aqueous iron corrosion at neutral and alkaline pH values (pH > 4.5) inevitably yields a complex oxide-film that shields the Fe⁰ surface (SCHMUKI 2002 and references therein), possibly rendering it inaccessible for contaminants (NOUBACTEP 2003, 2006a, 2006b, 2007). Furthermore, in a Fe⁰-H₂O system several other redox couples of iron species [Fe^{III}_(aq)/Fe^{II}_(aq), Fe^{III}_(s)/Fe^{II}_(s), Fe^{III}_(org)/Fe^{II}_(org)] may exist, which are possibly more powerful for contaminant reduction than the couple Fe^{II}/Fe⁰ (NAKA *et al.* 2006, WHITE & PATERSON 1996), and have the advantage of being more readily accessible than the underlying Fe⁰ surface. Thus, the spatial disposition of potential reductants in a Fe⁰-H₂O system is the first argument against the well-established premise of quantitative con-

taminant reduction at the Fe^0 surface (NOUBACTEP 2003, 2006a, 2006b, NOUBACTEP *et al.* 2006). As many other instances of scientific innovation (SCHMUKI 2002), the technical understanding (the know-how) preceded scientific understanding (the know-why) of contaminant removal in Fe^0 - H_2O systems. Understanding the real mechanisms of contaminant removal in the presence of Fe^0 materials (e.g. in Fe^0 - H_2O systems) is indispensable for the further development of the reactive wall technology.

In investigating contaminant removal by Fe^0 materials using batch experiments, mixing is mostly considered as a helpful tool to facilitate the transport of contaminants from the bulk solution to the Fe^0 surface (e.g. AGRAWAL & TRATNYEK 1996). However, it has been reported, that mixing operations are capable of disturbing processes in Fe^0 - H_2O systems (BÜCHLER *et al.* 1998, TOMASHOV & VERSHININA 1970). While trying to eliminate the diffusion as contaminant transport mechanism in synthetic Fe^0 - H_2O systems, the well-documented effects of the hydrodynamic on the formation and the characteristics of the oxide-film has therefore been mistakenly overseen. In this regard, BÜCHLER *et al.* (1998) investigated the formation, growth, and dissolution of the passive film on iron in neutral and alkaline solutions and found out that the strong influence of the hydrodynamic conditions can explain many contradictory literature results on the process. Similarly, NOUBACTEP *et al.* (2006) showed that mixing operations are responsible for contradictory results on the mechanism of uranium (VI) removal in Fe^0 - H_2O systems.

The aim of the present study is twofold: (a) further confirmation of the implausibility of the premise that quantitative contaminant reduction do occur at the Fe^0 surface; and (b) suggestion of better approaches to investigate processes in Fe^0 - H_2O systems for field applications. For this purpose the process of iron corrosion will be briefly recalled.

2 Behaviour of Metals in Aqueous Solutions

Under aqueous conditions an elemental metal (Me^0) may dissolve (solvation) to an oxidized metal cation (active corrosion or active dissolution) according to Eq. (1), or form a second phase film – usually an insoluble 3D surface oxide-film (passivation) – according to Eq. (2):

Active dissolution:



Passivation:



Active dissolution and passivation are competing reactions. A passive oxide-film will form whenever the metal solubility is low (circumneutral pH values). The further metal active 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. If the unit-cells of the metal and that of its oxides are very similar to one another, the oxides formed at the surface of the metal can adhere tightly to the uncorroded metal beneath it. In this way, the oxidized surface provides a protective layer that prevent water and other oxidants (solutes) from getting to the metal beneath. This is the case for example for Aluminium (DICKERSON *et al.* 1979).

In the case of iron, the unit-cells of the elemental element and its oxides are not particularly close (Table 1); thus there is no tendency for an iron oxide layer to adhere to metallic iron. In this regard, “the curse of rust is not that it forms, but that it constantly flakes off and exposes fresh iron surface” to the environment (DICKERSON *et al.* 1979; figure 1). Iron corrosion will normally continue until the material is depleted. The main reason for this is that ‘rust’ (an oxide mixture) has a different crystal structure from the iron, and creates only a porous, poorly adherent layer (non-protective).

Table 1: Lattice parameters (a, b, c), structure and density of metallic aluminum, metallic iron and relevant corrosion products (metal oxides). Note that, beside the similarity in the structure and the lattice parameters of Al and Al₂O₃ (see text), Al₂O₃ has a higher density than Al. For iron the Fe is the most dense specie.

Substance	Structure	Density (g/cm ³)	lattice parameters (in Å) a	Substance b	Structure c
Al	cubic	2.70	4.05		
Al ₂ O ₃	cubic*	3.6	7.90		
Fe	cubic	7.86	2.866		
Fe(OH) ₂	trigonal	3.40	3.27		4.62
FeO (wüstite)	cubic	5.67	4.30		
FeOOH (gel)	cubic		8.37		
Fe ₃ O ₄ (magnetite)	cubic	5.175	8.396		
FeOOH (goethite)	orthorhombic	4.28	4.60	10.01	3.04
FeOOH (akageneite)	tetragonal	3.55	10.52		3.028
FeOOH (lepidocrocite)	orthorhombic	4.09	3.65	12.50	3.07
Fe ₂ O ₃ (hematite)	trigonal		5.035	13.72	5.26

* recent publications report an hexagonal structure for Al₂O₃. The cubic structure is given here as it was considered for a long time as the main reason for the protectiveness of Al₂O₃-films. For the discussion in this study it is sufficient to acknowledge that Al₂O₃ forms a protective film on Al.

3 Generation of Oxide-film on Iron

The formation of an oxide-film on a Fe⁰-material upon aqueous corrosion is characteristic for pH > 4.5 and depends further upon several parameters: reactivity of the Fe⁰-material, temperature, composition, and flow rate of the groundwater. These parameters determine the structure, the thickness and the porosity of the generated film. Such films grow by counter migration of Fe²⁺ ions from the Fe⁰ surface (outward migration) and H⁺, O₂, and other solutes from the flowing groundwater (inward migration). Fe³⁺ ions are generated, migrate, precipitate and possibly reduce within the oxide-film. The driving forces for species transport are mostly electromigration (ionic species) and concentration gradient (all species). The films grow both at the metal/film interface and the film/electrolyte interface.

The reaction scheme for film formation can be divided into four steps: (i) active dissolution (Eq. 1), (ii) transition range, (iii) pre-passive range, and (iv) oxide-film formation (SCHMUKI 2002). In the transition and pre-passive range the metal becomes progressively covered by Fe(OH)_n adsorbates. These adsorbates increasingly block the active dissolution. The oxide-film is subsequently formed when the Fe⁰ is completely covered with Fe(OH)_n and deprotonization leads to the formation of a layer of iron oxides. 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 (SCHMUKI 2002). 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. PO₄³⁻) in groundwater may favour 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. In this case Fe⁰ active dissolution will continue until the material is depleted.

As already discussed, Fe⁰ materials own their suitability for groundwater remediation to the fact that the oxide-film continually flakes off and exposes the Fe⁰ surface to the corrosive aqueous environment. However, new films are suddenly generated such that the bare Fe⁰ surface can not be accessible for contaminant as a rule. In fact, all contaminants interact more or less strongly with the overlaying iron oxides. How can such a system be properly investigated?

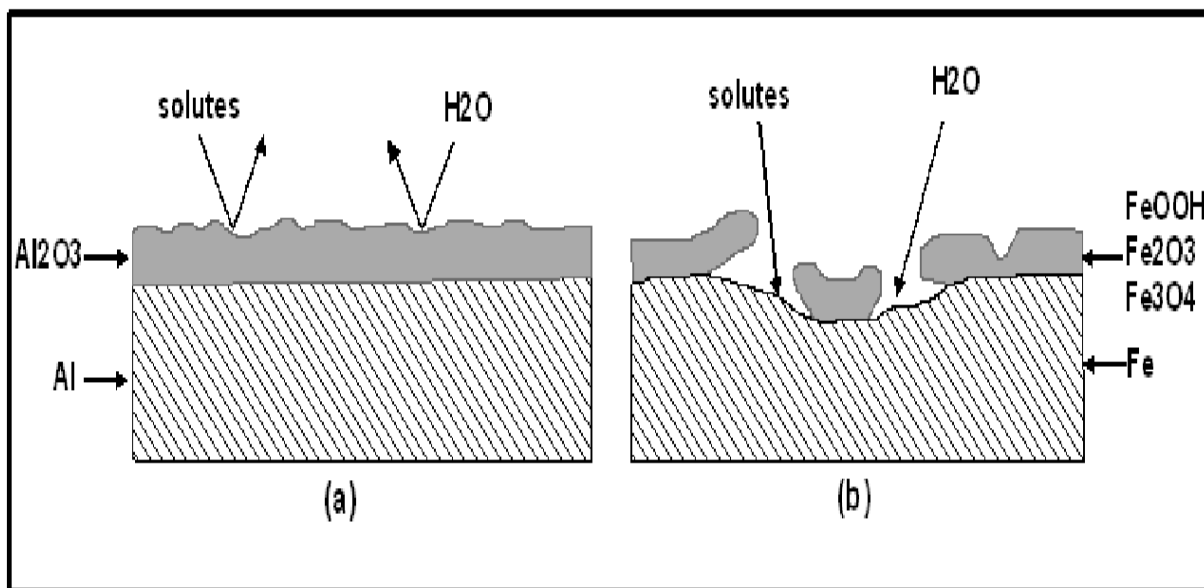


Figure 1: Schema of the growth of oxide-films on aluminium and iron: (a) A layer of Al_2O_3 , once formed, adheres to the surface of Al and protects it against further corrosion. (b) Iron oxides do not adhere as well to an iron surface. The oxide-layer continually flakes away as rust and exposes a clean surface to further attack by water and solutes. (modified after DICKERSON *et al.* 1979).

4 Investigating Contaminant Removal in $\text{Fe}^0\text{-H}_2\text{O}$ systems

The discussion above has shown clearly that 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, but rather two interfaces:

- $\text{Fe}^0/\text{oxide-film}$, and
- $\text{oxide-film}/\text{water}$.

Even though the metal surface may be temporally accessible at locations where the oxide-film is discontinued, this can not be a rule. Therefore investigations regarding contaminant removal in $\text{Fe}^0\text{-H}_2\text{O}$ systems should always be conducted under conditions favouring the generation of an oxide-film. Ideally, this is obtained under stagnant conditions. Under stagnant conditions, the mass transfer rate is less than the dissolution rate of the Fe^0 material into the aqueous solution, and the corrosion rate is determined by the mass transfer rate. For these cases, the corrosion product concentration at the initial $\text{Fe}^0/\text{H}_2\text{O}$ interface equals the saturation concentration, and precipitation reactions occur at the Fe^0 surface yielding an oxide-film. Beside stagnant conditions, another promising experimental procedure was proposed by DEVLIN *et al.* (1998) and involves the use of a glass-encased magnet reactor in a sealed beaker. In this procedure a granular Fe^0 sample remains stationary while the solution is stirred. In this manner, slowly stirring overcomes the kinetics of mass transfer while corrosion

products are not swept from Fe^0 surface. By carefully selecting the stirring speed, real field conditions can be closely simulated.

Decades of intensive investigation regarding the impact of diverse parameters on the process of iron corrosion has not univocally identified corrosive factors (MERCER & LUMBARD 1995, WILSON 1923). As the presence of contaminants (as one of the solutes) is solely one of the factors influencing iron corrosion and oxide-film formation, contaminant removal by an Fe^0 material can be regarded as the influence of the specific contaminant on the reference system $\text{Fe}^0\text{-H}_2\text{O}$ (active dissolution and passivation). This suggestion is supported by experimental results on the successful removal of Cr(VI) and Zn(II) in $\text{Fe}^0\text{-H}_2\text{O}$ systems. In fact, Cr(VI) is known for its passivating characteristics for iron materials whereas Zn(II) can not be electrochemically reduced by Fe^0 . Therefore, systematic long-term non-disturbed batch experiments could be a better approach for investigating processing in $\text{Fe}^0\text{-H}_2\text{O}$ systems. The author has been using this approach for more than seven years, with experimental durations varying from two weeks to up to four months using tap water as background solution. Unlike deionised water, tap water is a complex matrix which is closer to natural waters than any synthetic salt solution (MERCER & LUMBARD 1995). In non-disturbed batch experiments, the chemical dynamic of $\text{Fe}^0\text{-H}_2\text{O}$ systems can be modified by the addition of other

reactive materials (FeS₂, MnO₂, CaMg(CO₃)₂) (NOUBACTEP *et al.* 2005A, 2006).

Rather than assessing relevant processes (contaminant removal, oxide-film characteristics...) in individual Fe⁰-H₂O systems, the proposed approach qualitatively assesses the relative reactivity of a given Fe⁰-H₂O system as influenced by different contaminants while using a contaminant free system as reference. Such comparisons are helpful both in discussing the long-term reactivity of Fe⁰ materials and in identifying the effect of individual contaminant on the oxide-film generation and transformation. This approach has the additional advantage of using natural matrixes rather than synthetic solutions and thus closely mimics field conditions.

5 Concluding Remarks

The mechanism of iron corrosion (rusting) has been intensively discussed since the era of Aristotle (cited by SCHMUKI 2002). In the past two or three centuries important scientific investigations have dealt with the role of oxide-film in influencing species (mostly molecular oxygen) transport to the iron surface (e.g. STRATMANN & MÜLLER 1994). In all these efforts oxide-films on iron have been considered as physical barriers, whose properties (composition, thickness, porosity) change with time (SCHMUKI 2002 and references therein). In studies regarding the processes of contaminant removal in Fe⁰-H₂O systems, this evidence is only poorly reflected. Here, a disproportionately high attention is paid to the nature of oxide layers which are mostly considered as "coatings". With respect to contaminant removal processes however, oxide coatings are "dead" and can only remove contaminant through adsorption. Under natural conditions, oxide-films continually grow onto the metal at the interface Fe⁰/oxide-film while being simultaneously destroyed by dissolution or restructuring at the interface oxide-film/groundwater (SCHMUKI 2002).

Irrespective from the presence of any contaminant, processes involved in the oxide-film transformation included (but are not limited to):

- chemical, electrochemical or microbial Fe⁰ active dissolution;
- transport of solutes (Fe²⁺, Fe³⁺, H⁺, O₂) within the film;
- abiotic or biotic reduction of Fe^{III} to Fe^{II};
- species adsorption onto iron oxides,

- species co-precipitation with iron oxides, and
- oxide and hydroxide precipitation and recrystallisation.

Therefore, an alternative way to investigate the mechanism of contaminant removal in a given Fe⁰-H₂O system is to characterize the behaviour of such a system as influenced by various contaminants under near-natural conditions. Thereby, needless mixing operations should be avoided, used Fe⁰ loadings should not be too large and the experimental durations should exceed some days. Such an experimental design has been successfully applied to elucidate the mechanism of uranium removal in Fe⁰-H₂O systems (NOUBACTEP 2003, NOUBACTEP *et al.* 2003, 2005B, 2006).

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