Metallic iron for environmental remediation: ending a myth

Iron corrosion is widely known as a destructive process. However, several useful applications of this process are known. Three examples are: consumption of humidity in food packaging, H_2S removal from biogas and water treatment. Water treatment by metallic iron (Fe^0) relies on producing iron corrosion products (hydroxides/oxides) for contaminant adsorption, co-precipitation and adsorptive size-exclusion. The same process occurred during electrocoagulation where iron hydroxides/oxides production is sustained by an electric power. A popular example for using Fe^0 for water treatment is known from the aquaculture where steel wool has been long routinely used for phosphate removal. Corroding Fe^0 for generating iron hydroxides/oxides is thus an established tool for water treatment as these phases readily remove several aqueous chemical and biological contaminants. A relative new branch of science exists regarding Fe^0 as a reducing agent for contaminant degradation under environmental conditions. This seemingly scientific knowledge is already disseminated in lexica (including wikipedia) and textbooks. The fallacy of this view is demonstrated herein.

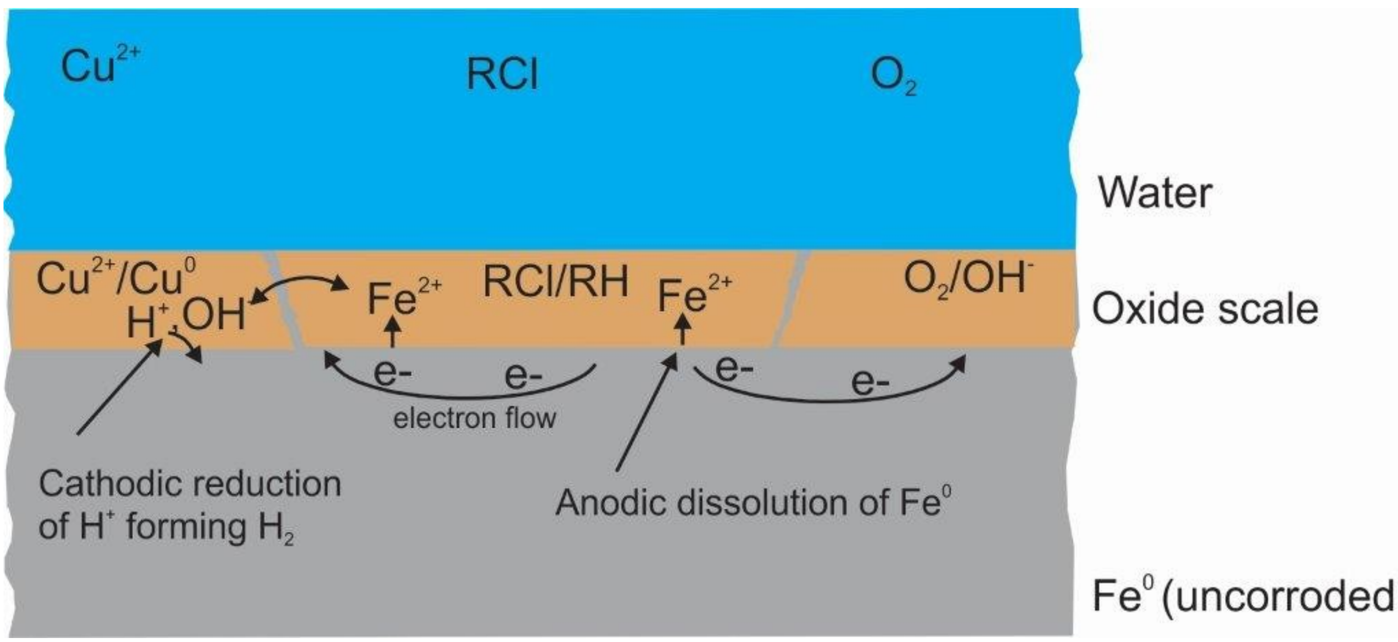

Fig. 1, Overview of a Fe^0/H_2O system labelling key features relevant for contaminant removal. Corrosion begins at a location where Fe^{2+} is generated (anode). Fe^{2+} goes into the aqueous solution and two electrons, left behind migrate to another location (cathode) where they are taken up by H+ from water dissociation (H_2O H+ + OH-). The resulting hydroxide ions (OH^-) react with the Fe^{2+} to initially form hydrous iron oxides ($Fe(OH)_2$) that precipitate. Depending from the environmental conditions $Fe(OH)_2$ is oxidized and transformed to various Fe^{II}/Fe^{III} oxides that form the oxide scale. The dynamic process of $Fe(OH)_2$ formation and transformation continues ideally until Fe^0 is depleted.

The Fe^0 filtration technology for environmental remediation was born with the observation that aqueous chlorinated hydrocarbons (RCl) disappeared from Fe^0-based canisters. This experimental observation was characterized as a chemical reduction (degradation) and corresponding reaction products were identified. No particular attention was paid to the molar ratio Fe^0:RCl in presence. During the past 25 years, intensive efforts were undertaken to optimize the efficiency of Fe^0-based filtration systems (Fe^0 filters). However, related efforts were mostly based on the premise that electrons from the Fe^0 body are transferred to dissolved species (direct reduction) despite the presence of an oxide scale (Figure 1). The universal oxide scale has been widely described as a shield protecting the Fe^0 surface from ‘aggressive’ dissolved electron acceptors.

Location	Reaction	Nature	Eq.
Fe^0 surface	$Fe^0 \Rightarrow Fe^{2+} + 2\ e^-$	Anodic	(1)
Fe^0 surface	$2\ H^+ + e^- \Rightarrow H_2$	Cathodic	(2)
Oxide scale	$O_2 + 2\ H_2O + 4\ e^- \Rightarrow 4\ OH^-$	Cathodic	(3)
Oxide scale	$Cu^{2+} + 2\ e^- \Rightarrow Cu^0$	Cathodic	(4)
Oxide scale	$RCl + 2\ e- + H^+ \Rightarrow RH + Cl^-$	Cathodic	(5)
Fe^0 surface	$Fe^0 + 2\ H^+ \Rightarrow Fe^{2+} + H_2$	Electrochemical	(6)
Fe^0 surface	$2\ Fe^0 + O_2 + 2\ H_2O \Rightarrow 2\ Fe^{2+} + 4\ OH^-$	Electrochemical	(7)
Fe^0 surface	$Fe^0 + Cu^{2+} \Rightarrow Fe^{2+} + Cu^0$	Electrochemical	(8)
Fe^0 surface	$Fe^0 + RCl + H^+ \Rightarrow Fe^{2+} + RH + Cl^-$	Electrochemical	(9)
Oxide scale	$4\ Fe^{2+} + O_2 + 2\ H_2O \Rightarrow 4\ Fe^{3+} + 4\ OH^-$	Chemical	(10)
Oxide scale	$2\ Fe^{2+} + Cu^{2+} \Rightarrow 2\ Fe^{3+} + Cu^0$	Chemical	(11)
Oxide scale	$2\ Fe^{2+} + RCl + H^+ \Rightarrow 2\ Fe^{3+} + RH + Cl^-$	Chemical	(12)

Table 1. Key reactions relevant for the process of contaminant removal in Fe^0/H_2O systems. Cu^{2+}, O_2 and RCl are examples of reducible species (oxidizing agents). Fe^{2+} reacts with hydroxide ions from water dissociation to form the oxide scale. Because this scale is typically electronic non conductive, quantitative electrochemical reduction of dissolved species (red-marked) is not possible. The sole likely quantitative electrochemical process is iron corrosion by water (H^+) (blue-marked). Contaminant are removed within the oxide scale. Chemical reduction (degradation) is not a removal mechanism at ug/L-level as it is not quantitative. On the other hand, reduced species must be removed from the aqueous phase as well.

Table 1 summarizes the chemical reactions relevant for the discussion of the process of contaminant reduction and removal in Fe^0/H_2O systems. The most probable location of their occurrence is also specified. The fundamental reaction is the Fe^0 oxidative dissolution (Eq. 1). Eq. 1 describes the anodic process in the electrochemical corrosion of Fe^0. It is known, that this anodic reaction is facilitated by the presence of suitable electron acceptors (oxidizing agents). Oxidizing agents in Tab. 1 are: protons (H^+ - Eq. 2), dissolved O_2 (Eq. 3), Cu^{2+} ions (Eq. 4), and RCl (Eq. 5). The electrochemical cells corresponding to the four electron acceptors are given in Eq. 6 through Eq. 9. Of these only Fe^0 corrosion by water (H^+) is certain because the oxide scale is typically non conductive. This makes the oxide scale a conductive barrier for electrons and a physical barrier for dissolved species. In other words, aqueous contaminants are reduced in a Fe^0/H_2O system by a pure chemical mechanism according to Eq. 10 through Eq. 12. This conclusion alone ends the myth of reductive transformations by Fe^0 (electrons from Fe^0).

The myth of reductive transformation by Fe^0 has attempted to challenge mainstream iron corrosion science for 25 years. It was questioned at the introduction and during its whole lifetime. The wished contaminant degradation, achieved in the presence of Fe^0, was constantly presented as proofs of concept. From 2006 on, the mistaken view has been systematically dismantled by a series of arguments which are supported since 2011 by sound experimental data. To date, some five research groups have realized the fallacy of the ‘reductive transformation concept’ worldwide. The alternative concept has already established (i) the ion-selective nature of Fe^0 filters and (ii) some tools for the proper design of Fe^0 filters.

Chicgoua Noubactep

Angewandte Geologie, Universität Göttingen, Germany.

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