

Processes of Contaminant Removal in “Fe⁰-H₂O” Systems Revisited: The Importance of Co-Precipitation

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Abstract: The mechanism of aqueous contaminant removal by elemental iron (Fe⁰) materials (e.g., in Fe⁰-H₂O systems) has been largely discussed in the “iron technology” literature. Two major removal mechanisms are usually discussed: (i) contaminant adsorption onto Fe⁰ oxidation products, and (ii) contaminant reduction by Fe⁰, Fe^{II} or H/H₂. However, a closer inspection of the chemistry of the Fe⁰-H₂O system reveals that co-precipitation could be the primary removal mechanism. The plausibility of contaminant co-precipitation with iron corrosion products as independent contaminant removal mechanism is discussed here. It shows that the current concept does not take into account that the corrosion product generation is a dynamic process in the course of which contaminants are entrapped in the matrix of iron hydroxides. It is recalled that contaminant co-precipitation with iron hydroxides/oxides is an unspecific removal mechanism. Contaminant co-precipitation as primary removal mechanism is compatible with subsequent reduction and explains why redox-insensitive species are quantitatively removed. Adsorption and co-precipitation precede reduction and abiotic reduction, when it takes place, occurs independently by a direct (electrons from Fe⁰) or an indirect (electrons from Fe^{II}/H₂) mechanism.

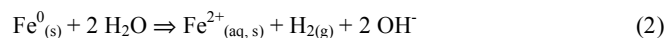
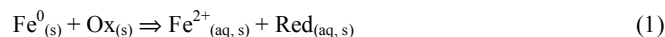
INTRODUCTION

A concept is proposed for evaluating aqueous contaminant removal in the presence of elemental iron or zero-valent iron materials (e.g., in Fe⁰-H₂O systems) by adsorption, precipitation, co-precipitation, and chemical reduction that is consistent with published experimental observations. *Adsorption* refers to the accumulation of solute molecules on the surface of a solid (Fe⁰, iron hydroxides/oxides). *Precipitation* refers to the spontaneous formation of precipitates from electrolyte solutions. *Co-precipitation* refers to the entrapment of foreign species in the matrix of precipitating compound (e.g. contaminants in iron hydroxides/oxides). *Chemical reduction* refers to a reaction in which a chemical species (contaminant) gains one or more electrons (its oxidation number decreases). *Co-precipitation* is sometimes referred to a specific chemical reaction in a multi-component system, for example a ternary system Fe-Cr-O yielding (Cr_xFe_{1-x})(OH)₃ (s) or Cr_xFe_{1-x}OOH (s). The specific feature of this co-precipitation is that the chemical reaction is rendered possible by the similitude between the atom radii of the involved metal ions. *Co-precipitation* as considered in the present study is an unspecific removal mechanism in which foreign species (contaminants, nutrients, viruses) are simply entrapped in the matrix of precipitating or recrystallizing iron hydroxides/oxides.

Evaluating the relative importance of the individual mechanisms in the process of contaminant removal is essential for the proper engineering of iron remediation technologies. For instance, if reduction is the main reaction path and a surface-mediated process, it can reasonably be assumed that transport of the contaminant of interest to the iron surface will be the rate-limiting step in many treatment scenarios [1].

The currently widely accepted concept for contaminant removal results mostly from Weber’s work [1] who re-evaluated a seminal work of Matheson & Tratnyek [2]. Weber’s main conclusion is that the reductive transformation (implicitly considered as main removal path) by Fe⁰ is “a surface-mediated process which requires that the substrate (Ox in Eq. 1) of interest contact the iron surface for electron transfer to take place”.

The first problem with this concept (referred to here as the MTW concept – Matheson-Tratnyek-Weber concept) is that appropriate water-soluble electron mediators must be present to guarantee electron transfer. Even though such “electron mediators” are likely to be present in soils [1, 3], the contaminant of interest is usually not the controlling Fe⁰ oxidizer [4, 5], as other species (including H₂O, Eq. 2) are present in greater stoichiometric abundance.



The second problem with the MTW concept is that it differentiates between organics which are removed *via* reductive degradation and inorganics which are possibly removed by surface adsorption *via* electrostatic attraction, surface complexation [6], or (co)precipitation. These three removal paths may be coupled to redox reactions for redox-active species [7]. This segregation between organics and inorganics is arbitrary as organics (reactants and products) are known to adsorb onto iron oxides [8, 9].

The major problem of the MTW concept is that it can not explain why non-reducible species such as zinc [10, 11], triazoles [12], and even viruses [13] are quantitatively removed in Fe⁰-H₂O systems.

The objective of this study is to show that the MTW concept is not stable. Many scientists may accept a concept

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similar to the one suggested here. However, no published literature has been found pointing out the inconsistency between the MTW concept and quantitative removal of redox-insensitive contaminants. The revised concept proposed here is valid for ionic, neutral, organic, inorganic, reducible and non-reducible compounds (including contaminants). Such a concept considers Fe^0 as generator of an oxide film which adsorbs all species and entraps them in its structure while ageing. Unspecific contaminant co-precipitation as removal mechanism enables a better discussion of published data.

THE MTW CONCEPT AND ITS LIMITATIONS

The MTW concept is described in several recent works [5, 14, 15]. From the discussion above, the MTW concept suggests that Fe^0 serves as reducing agent for a contaminant (direct reduction) and the oxide film serves as catalyst for indirect reduction through adsorbed Fe^{II} (structural Fe^{II} or $\text{Fe}^{\text{II}}_{(\text{s})}$) or H_2 [2]. It is obvious that the dynamic nature of film formation is not considered at all. Hence, the oxide film is treated as a coating. However, regardless of the presence of any contaminant and the composition of groundwater, an oxide film grows, and its porous structure and composition changes with time [16].

The MTW concept is widely accepted in current literature despite four strong features suggesting its instability: (i) the concept is derived without demonstration/verification from the thermodynamic standpoint (low reduction potential of the redox couple $\text{Fe}^{\text{II}}/\text{Fe}^0$), (ii) a number of publications has attempted to point out its instability for individual contaminants [17-20], (iii) the MTW concept is inadequate to explain some experimental results as will be shown later, and (iv) where the concept is believed to have been demonstrated the experimental conditions were not appropriate [21-24]. In particular, the experimental conditions of Matheson & Tratnyek [2], and Weber [1] are not sufficient to allow traceable conclusions.

Matheson & Tratnyek [2] used a pre-equilibration period of 8-12 h during which the Fe^0 - H_2O system was shaken on a rotary shaker (15 rpm) prior to the contaminant addition. During this period iron hydroxides/oxides were quantitatively produced to allow catalytic reduction by structural Fe^{II} . Clearly, in producing iron oxides prior to contaminant addition, Matheson & Tratnyek [2] created favourable conditions for a concurrent reaction: the indirect reduction.

Weber [1] used an azo dye (4-Aminoazobenzene) to demonstrate that the reduction with Fe^0 is surface-mediated at pH 7.2. The reduction of azo dyes by Fe^0 is industrially well-known for the synthesis of aniline after the Béchamp reaction [25-28]. The reduction is known to take place in the presence of Fe^0 and dilute acid [27] and the yield of the reaction is commonly less than 92 % of the theoretical amount [26, 28]. The investigations of Weber [1] were performed in analogy to more recent works on the reductive degradation of organic compounds [2, 4, 29, 30] and the 150 years old work of Béchamp was not considered. Given the possible differences in Fe^0 - H_2O systems at pH 4 and pH 7 (e.g., contaminant speciation, kinetics of Fe^0 corrosion), Weber [1] did not explained why a reaction, which is not quantitative in industrial reactors at pH 4, should be quantitative in the environment at pH 7.2.

In summary, the validity of the well-accepted MTW concept has not been demonstrated by any scientific criterion. It failed to explain experimental observations in many cases as will be shown below.

EXPERIMENTAL OBSERVATIONS

Evidence contradicting the MTW concept is abundant in the literature. In this section six relevant examples will be considered:

In many cases, aqueous contaminant removal has been reported to occur after a lag time [18, 31-33]. Such lag time is often seen in biological systems if the initial population of bacteria is small, or if synthesis of the appropriate enzymes must be induced [33]. In Fe^0 - H_2O systems the observed lag time can be regarded as the time necessary for the generation of enough corrosion products for contaminant co-precipitation [18-20]. This explanation is supported by the pH-dependence of the lag time as reported by Huang *et al.* [32] for nitrate removal. In fact these authors observed a lag time of a few minutes at pH 4.0, and no lag time at pH 2.5. Iron is essentially more soluble at pH 2.5 than at pH 4.0. In other words, iron precipitation and thus contaminant co-precipitation is more likely at pH 4.0.

Qui *et al.* [34] investigated the removal of selenium (Se^{VI}), chromium (Cr^{VI}), and uranium (U^{VI}) by Fe^0 . According to the MTW concept all these reducible species should have been reduced to Se^{IV} , Cr^{III} and U^{IV} respectively. Qui *et al.* [33] reported that partially reduced Se^{IV} and Cr^{III} are adsorbed on the Fe^0 surface, while uranium is deposited without reduction (U^{VI}). All species were quantitatively removed from the aqueous solution.

Lavine *et al.* [17] investigated the process of nitrobenzene reduction by Fe^0 while simultaneously monitoring the disappearance of nitrobenzene and the appearance of Fe^{II} . Their studies proved informative but were unable “to access information about crucial mechanistic details on the chemical processes controlling the reduction of nitrobenzene at the Fe^0 surface” [17].

Rademacher *et al.* [35] investigated the process of uranium(VI) removal by Fe^0 by means of isotope fractionation and reported that “ Fe^0 reduced U^{VI} , but the reaction failed to induce an analytically significant isotopic fractionation”. This obviously questionable conclusion was consistent with the MTW concept and the results of Gu *et al.* [36] on reductive precipitation of U^{VI} by Fe^0 . However, other researchers [18-20] could demonstrate that U^{VI} removal by Fe^0 is primarily the result of U^{VI} co-precipitation with iron corrosion products. The example of U^{VI} removal by Fe^0 shows that the uncritical acceptance of the MTW concept has led to misinterpretations of good experimental results.

In an attempt to explain the perchlorate (ClO_4^-) removal by Fe^0 , Huang & Sorial [14] referred to their carbon content (ca. 3 % in cast iron) in analogy to adsorption onto activated carbon. An important feature pointed out by the authors in their discussion of ClO_4^- removal is the differential behaviour of breakthrough profiles for activated carbon and Fe^0 . In fact, in column experiments with activated carbon [37], once ClO_4^- was detected in the effluent, the effluent concentration reached the level of influent concentration immediately. By contrast, the effluent ClO_4^- concentration in Fe^0 column ex-

periments remained stable even after 30 days of first perchlorate appearance. Huang & Sorial [14] interpreted this result as ClO₄⁻ reduction by Fe⁰. The next section will show that ClO₄⁻ co-precipitation (not considered by the authors) is an equally plausible removal mechanism.

Jia *et al.* [12] investigated the adsorption of triazoles by iron hydroxides/oxides (Fe₂O₃, ferrihydrites) and elemental iron. Their data suggest negligible adsorption of triazoles onto Fe₂O₃ and strong adsorption of triazoles onto ferrihydrites. The adsorption onto Fe⁰ was the strongest and reported to be controlled by multi-layer coverage. Interestingly, the used triazoles are redox-insensitive and all tested iron hydroxides/oxides are likely to be present in a Fe⁰-H₂O system. The question arises why reduction through Fe⁰ should be the major removal reaction path when the contaminant is redox-sensitive.

The selected experimental evidence indicates that the MTW concept is unsatisfactory. A revised concept is described below. For this purpose, the process of contaminant co-precipitation with corrosion products will be first presented.

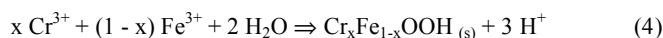
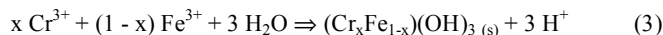
THE PROCESS OF CONTAMINANT CO-PRECIPI-TATION WITH CORROSION PRODUCTS

Whenever a specie (e.g., iron) precipitates (e.g., as hydroxide) in the presence of trace amounts of foreign species, the foreign species are entrapped in the mass of precipitates (co-precipitation). Co-precipitation is a well-known unspecific specie removal mechanism from the aqueous solution [38-40].

Depending on the redox conditions, Fe⁰ aqueous oxidative dissolution yields a large array of porous and highly adsorptive iron hydroxides (e.g., Fe(OH)₂, Fe(OH)₃, ferrihydrites), which are further transformed upon dehydration and crystallisation into various less porous and less adsorptive oxides (e.g., Fe^{II}O, Fe^{II}Fe^{III}O₄, Fe^{III}OOH, Fe^{III}₂O₃). The precipitation proceeds by succession and interplay of several precipitation processes, i.e., nucleation, growth, aggregation (or stabilization), and ageing [39, 40]. In a contaminant-free Fe⁰-H₂O system (e.g., early phase of barrier installation), homogeneous nucleation occurs. Three-dimensional pure phase nuclei are formed from a homogeneous parent phase in the vicinity of Fe⁰ [16]. In the presence of contaminants, heterogeneous nucleation occurs. Here, contaminants are progressively incorporated in the structure of growing nuclei. The relative extent of homogeneous and heterogeneous nucleation in a Fe⁰-H₂O system depends on the contaminant concentration and flux (water flow velocity).

Since immersion of reactive Fe⁰ always yields an oxide film and oxide film formation is a dynamic process [16], Fe⁰ can be considered a source of continuously growing substrate of iron oxide for contaminant removal. As the substrate contains hydroxides and oxides of various porosity and crystalline structure, it possesses at any time variable sorption vs co-precipitation efficiency for contaminants. However, at time scales pertinent to laboratory batch experiments (hours to a few days), contaminant co-precipitation with precipitating corrosion is very likely to dominate simple adsorption. It is rather surprising that co-precipitation as primary (and independent) contaminant removal mechanism has not been discussed in seminal works [1, 2].

Note that co-precipitation as discussed for example for chromium (Cr) (Eq. 3, Eq. 4; cf. ref. [41, 42]) is a specific chemical reaction. Co-precipitation as presented in this study is an unspecific removal mechanism, which can be schematically written as shown in Eq. 5, and Eq. 6.



In all the cases Cr is removed from the aqueous solution. In Eq. 3, and Eq. 4 Cr^{VI} is first reduced to Cr^{III}. Equations 5 and 6 show that both Cr^{III} and Cr^{VI} may be entrapped in the structure of growing iron hydroxides (unspecific mechanism).

Generally, a co-precipitated oxidized contaminant (e.g., Cr^{VI}) can be further reduced (e.g., to Cr^{III}). The question arises whether a reduction precedes co-precipitation or vice versa. As available experimental evidence shows that even redox-insensitive species are co-precipitated, there is no reason why reduction should precede co-precipitation as a rule.

REVISED CONCEPT

The proposed concept treats adsorption and co-precipitation as the primary removal mechanism of any species (ionic, neutral, organic, inorganic, and living) in a Fe⁰-H₂O system and explains why a wide array of species is successfully removed from the aqueous phase. A redox-sensitive specie, can be subsequently reduced by electrons from Fe⁰, from structural Fe^{II} or H/H₂. Some features of the MTW concept are still valid, in particular that the oxide-film may serve as catalyst (for indirect reduction) and Fe⁰ as electron donors (for direct reduction).

The key difference between the proposed concept and the MTW concept lies in the role of the oxide film on the Fe⁰ surface. The MTW concept considers the oxide film as electron mediator [6], limiting indirect reduction to a side effect. The revised concept considers the growing oxide film as contaminant scavenger, such that contaminant reduction should not be necessarily seen as surface-mediated (the surface been that of Fe⁰). Furthermore, it is yet to be discussed in the case of contaminant reduction, which mechanism from the direct (electrons from Fe⁰) and the indirect reduction (electrons from Fe^{II}/H₂) is likely to be dominant.

A logical consequence of the revised concept is that experiments investigating the process of contaminant removal should be conducted under conditions favouring the generation and transformation of oxide films on the Fe⁰ surface. Particularly mixing operations (type and intensity) should be proven non-disturbing before being employed.

Co-precipitation as primary contaminant removal mechanism explains all the above enumerated experimental observations. In particular, in the columns experiments of Huang & Sorial [14] it is likely that the described 30 days stable effluent ClO₄⁻ concentration corresponds to a steady state regime in the process of Fe⁰ oxidation in the column, yielding a constant amount of corrosion products for ClO₄⁻ co-precipitation.

CONCLUDING REMARKS

A concept providing evidence for quantitative contaminant removal by co-precipitation with iron corrosion products is presented. It argues that adsorbed contaminants are co-precipitated with aging corrosion products. This concept is consistent with many experimental observations and is valid irrespective from (i) the redox conditions (oxic or anoxic), and (ii) the nature of the contaminant (ionic, neutral, organic, inorganic, redox sensitive, redox insensitive).

The present work has shown that generated corrosion products are primarily responsible for the process of contaminant removal in Fe⁰-H₂O systems. Thus, a contaminant can only migrate across a Fe⁰ bed (or barrier) if the adsorptive capacity of actual available corrosion products is exhausted. In an operative barrier both adsorption onto aged corrosion products, and co-precipitation with nascent iron oxides occur. Corrosion products form an active physical barrier reducing the accessibility of the bare surface of Fe⁰ materials to contaminants. This assertion is supported by experimental evidence from Huang and Zhang [43] who showed that dissolved oxygen is mostly consumed by Fe^{II} rather than the surface of metallic iron (Fe⁰). Therefore, reported contaminant reduction in Fe⁰-H₂O systems may mostly result from structural Fe^{II} reaction and/or microbial activity. The verification of this hypothesis is a challenge for the scientific community. Moreover, the discussion of the stability of co-precipitated contaminants as influenced by relevant environmental factors (groundwater biogeochemistry, groundwater flow velocity) is urgently needed to access the stability of removed contaminants and the long-term performance of Fe⁰ reactive walls.

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