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Letter to the Editor

On the operating mode of bimetallic systems for environmental remediation

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ABSTRACT

This letter challenges the concept that Fe⁰/Me⁰ bimetallic systems enhance contaminant reduction on Me⁰ surfaces. It is shown on a pure thermodynamic perspective that any enhancement of contaminant reduction by Fe⁰ in the presence of a second more electropositive elemental metal (Me⁰) is the result of an indirect process resulting from iron corrosion. This demonstration validates the concept that aqueous contaminant removal in the presence of Fe⁰ mostly occurs within an in situ generated oxide film on Fe⁰.

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A metallic surface can be involved in chemical reactions in various ways: a metallic material can serve as a redox agent or catalyst, facilitating a reaction, or it can release metal species into the system [1,2]. Elemental iron (Fe⁰) and Fe⁰/Me⁰ bimetallic systems used in water remediation (Fe⁰-H₂O systems) are typical systems where all these three reaction paths might be involved: (i) Fe⁰ might serve as reducing agent (direct reduction), (ii) Fe⁰ surface might serve as catalyst for instance for the reduction through molecular (H₂) or atomic hydrogen (H) and (iii) Fe⁰ might release Fe^{II} and H/H₂ into the system. A Fe⁰/Me⁰ system is a system where the metallic surface should serve as a catalyst for contaminant reduction through hydrogen (H/H₂).

A survey of the voluminous literature on environmental remediation with Fe⁰ shows that all factors increasing Fe⁰ oxidation enhance contaminant removal. These factors include (i) the presence of molecular oxygen [3], (ii) the addition of a second more electropositive metal (e.g. Ag⁰, Co⁰, Cu⁰, Ni⁰, Pd⁰, Pt⁰, Ru⁰) yielding bimetallic systems [4,5], and (iii) increasing the surface area of iron by reducing its particle size [4]. Increasing Fe⁰ oxidation is directly correlated with increased generation of iron corrosion products (e.g. iron oxyhydroxides) which are well-known for their adsorptive capacity for both organic and inorganic compounds [6,7]. Iron corrosion products are formed as an oxide film at the Fe⁰ surface. To reach the underlying Fe⁰ surface a contaminant molecule should migrate across the film.

In discussing aqueous contaminant removal in the presence of Fe⁰, reduction at the Fe⁰ surface and adsorption onto iron corrosion products have traditionally been evaluated as separate, independent processes that occur simultaneously or sequentially. Thereby the dynamic nature of the formation of the oxide film on Fe⁰ [8] has been almost overseen. However, during their formation and transformation iron corrosion products likely sequester foreign species, including contaminants [9]. Therefore, the author of ref. [9] has revisited the concept of reductive transformations [3,10] and introduced a new concept considering adsorption and co-precipitation of contaminants with iron corrosion products as fundamental removal mechanism. The present letter shows that the conception that bimetallic systems enhance reductive transformation by Fe⁰ is incompatible with the premise that Fe⁰ is the reducing

agent in Fe⁰-H₂O systems (*statement 1*). It has been reported that the presence of Pd⁰ speeds up the reduction reaction as follows: on the Pd⁰ surface, molecular hydrogen (H₂) from iron corrosion is adsorbed and dissociated into more reducing atomic H; atomic H attacks halogenated contaminants (RX) and transforms them to RH and X⁻ [11]. Therefore, the better well-dispersed the Pd⁰ in the Fe⁰/Pd⁰ system, the higher the catalytic effect. But, as recalled above, a universal oxide film shields the bimetallic surface [9,12]. Catalytic hydrodehalogenation is a well-known decontamination process [13]; it differs from the reductive dehalogenation reactions by Fe⁰ and Fe⁰/Pd⁰ systems in that the catalytic surface (Pd⁰) and the electron donor (H₂) are supplied as two separate reagents.

To demonstrate the absurdity of *statement 1*, let's consider the bimetallic system Fe⁰/Pd⁰ and a chlorinated hydrocarbon (RCl) to be reduced by the bimetallic. The involved electrode potentials (*E*⁰) are: 0.915 V for the couple Pd^{II}/Pd⁰, 0.41 to 0.59 V for the couple RCl/R⁻ [14], and -0.44 V for the couple Fe^{II}/Fe⁰. The higher the *E*⁰ value, the stronger the reducing capacity of Fe⁰ for the oxidant of a couple. Comparing the three *E*⁰ values, it is evident that Pd^{II} and RCl are concurrent oxidants for Fe⁰, Pd^{II} been the strongest. Therefore, if any RCl removal enhancement is observed in the presence of Pd^{II} it is indirectly related to Fe⁰ oxidation. Thus enhanced contaminant reduction by bimetallics [4,5,15] is an argument for indirect reduction (by Fe^{II} or H/H₂ within the oxide film on Fe⁰) [12]. Because of the omnipresence of the oxide film, even if the reducing agent is H/H₂, the reduction is not likely to occur at the Pd⁰ surface. On the other hand Fe^{II} adsorbed onto the oxide film (Fe^{II}_(s) or structural Fe^{II}) has been shown to be a very strong reducing agent [16].

For illustration, consider an ideal redox indicator for the titration of Fe⁰ by Pd^{II} (Eq. (1)) having a standard potential of 0.238 V. The redox half-reaction of the indicator is described by Eq. (2) [17], where Ind_{ox} is the coloured oxidized form of the indicator, Ind_{red} is the corresponding colourless reduced form, *n* is the number of electrons transferred (typically 1 or 2), and *m* is the number of protons transferred (typically 0, 1 or 2) and is dependent on the pH.





The end of the titration (Fe^0 depletion) is detected by the appearance of a colour in the solution. This colouration of the solution corresponds to the oxidation of the reduced form of the indicator to the oxidized form (Eq. (3)) by Pd^{2+} ions. To obtain accurate results, the lowest possible amount of indicator should be used. In the titration context, no one can claim that Pd^{II} enhances the reduction of Ind_{ox} by Fe^0 . Pd^{II} oxidizes both Ind_{ox} and Fe^0 . In this competition Fe^0 is the stronger electron donor. Therefore, if any Ind_{ox} reduction enhancement is observed in the presence of Pd^{II} , it can only indirectly be related to Fe^0 oxidation. It is true that the surface of Pd^0 and not dissolved Pd^{II} is the catalyst for contaminant reduction by H/H_2 . The Pd^0 surface is however, shielded as a rule, and dissolved Pd^{II} will (at least partly) co-precipitate with iron hydroxides and will no more be available for catalytic activity.

In conclusion, Pd^0 and other bimetallic elements (e.g. Co^0 , Cu^0 , Ni^0 , Pt , Ru^0) can not significantly enhance contaminant reduction by elemental iron (electron from Fe^0 or from H/H_2). Consequently, the reported increased contaminant removal by bimetallic systems is a result of secondary redox processes within the oxide film on Fe^0 (electron from Fe^{II} or from H/H_2). This conclusion is a further negation of the well-established concept of direct reductive transformations as major decontamination process [9,12].

For the further development of the iron reactive wall technology target experiments should be performed to investigate the influence of hydrodynamic shear stress on the transport, transfer and reaction rates within the oxide film, as well as film detachment under experimental conditions pertinent to natural situations. This means that experiments must be performed under conditions which favour oxide film formation and transformation. Redox processes within a film on iron is well documented in the context of microbiologically influenced corrosion [18].

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