1 **On the Operating Mode of Bimetallic Systems for Environmental**

2 **Remediation**

3 Noubactep C.

4 Angewandte Geologie, Universität Göttingen, Goldschmidtstraße 3, D - 37077 Göttingen, Germany.

5 e-mail: cnoubac@gwdg.de; Tel. +49 551 39 3191, Fax: +49 551 399379

6

7 **Abstract**

8 This letter challenges the concept that Fe^0/Me^0 bimetallic systems enhance contaminant

9 reduction on Me^0 surfaces. It is shown on a pure thermodynamic perspective that any

10 enhancement of contaminant reduction by Fe^0 in the presence of a second more

11 electropositive elemental metal (Me^0) is the result of an indirect process resulting from iron

12 corrosion. This demonstration validates the concept that aqueous contaminant removal in the

13 presence of Fe^0 mostly occurs within an in-situ generated oxide film on Fe^0.

14

16

17 A metallic surface can be involved in chemical reactions in various ways: a metallic material

18 can serve as a redox agent or catalyst, facilitating a reaction, or it can release metal species

19 into the system [1,2]. Elemental iron (Fe^0) and Fe^0/Me^0 bimetallic systems used in water

20 remediation (Fe^0-H_2O systems) are typical systems were all these three reaction paths might

21 be involved: (i) Fe^0 might serve as reducing agent (direct reduction), (ii) Fe^0 surface might

22 serve a catalyst for instance for the reduction through molecular (H_2) or atomic hydrogen (H)

23 and (iii) Fe^0 might release Fe^{II} and H/H_2 into the system. A Fe^0/Me^0 system is a system where

24 the metallic surface should serve as a catalyst for contaminant reduction through hydrogen
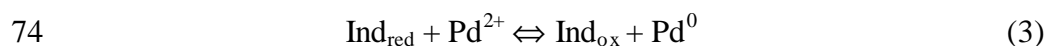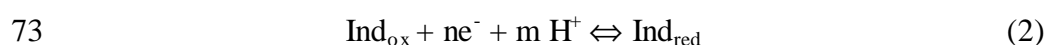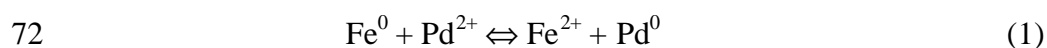
25 (H/H_2).

26   A survey of the voluminous literature on environmental remediation with Fe^0 shows that all

27   factors increasing Fe^0 oxidation enhance contaminant removal. These factors include (i) the

28   presence of molecular oxygen [3], (ii) the addition of a second more electropositive metal

29   (e.g. Ag^0, Co^0, Cu^0, Ni^0, Pd^0, Pt^0, Ru^0) yielding bimetallic systems [4,5], and (iii) increasing

30   the surface area of iron by reducing its particle size [4]. Increasing Fe^0 oxidation is directly

31   correlated with increased generation of iron corrosion products (e.g. iron oxyhydroxides)

32   which are well-known for their adsorptive capacity for both organic and inorganic compounds

33   [6]. Iron corrosion products are formed as an oxide film at the Fe^0 surface. To reach the

34   underlying Fe^0 surface a contaminant molecule should migrate across the film.

35   In discussing aqueous contaminant removal in the presence of Fe^0, reduction at the Fe^0

36   surface and adsorption onto iron corrosion products have traditionally been evaluated as

37   separate, independent processes that occur simultaneously or sequentially. Thereby the

38   dynamic nature of the formation of the oxide film on Fe^0 [8] has been almost overseen.

39   However, during their formation and transformation iron corrosion products likely sequestrate

40   foreign species, including contaminants [9]. Therefore, the author of ref. [9] has revisited the

41   concept of reductive transformations [3,10] and introduced a new concept considering

42   adsorption and co-precipitation of contaminants with iron corrosion products as primordial

43   removal mechanism. The present letter shows that the conception that bimetallic systems

44   enhance reductive transformation by Fe^0 is incompatible with the premise that Fe^0 is the

45   reducing agent in Fe^0-H_2O systems (**statement 1**). It has been reported that the presence of

46   Pd^0 speeds up the reduction reaction as follows: on the Pd^0 surface, molecular hydrogen (H_2)

47   from iron corrosion is adsorbed and dissociated into more reducing atomic H; atomic H

48   attacks chlorinated contaminants (R-X) and transforms them to R-H and Cl^- [11]. Therefore,

49   the better well-dispersed the Pd^0 in the Fe^0/Pd^0 system, the higher the catalytic effect. But, as

50   recalled above, an universal oxide film shields the bimetallic surface [9,12]. Catalytic

51   hydrodehalogenation is a well-known decontamination process [13]; it differs from the

52 reductive dehalogenation reactions by Fe^0 and Fe^0/Pd^0 systems in that the catalytic surface

53 (Pd^0) and the electron donor (H_2) are supplied as two separate reagents.

54 To demonstrate the absurdity of **statement 1**, lets consider the bimetallic system Fe^0/Pd^0 and

55 a chlorinated hydrocarbon (RCl) to be reduced by the bimetallic. The involved electrode

56 potentials (E^0) are: 0.915 V for the couple Pd^{II}/Pd^0, 0.41 to 0.59 V for the couple $RCl/R°$ [14],

57 and –0.44 V for the couple Fe^{II}/Fe^0. The higher the E^0 value, the stronger the reducing

58 capacity of Fe^0 for the oxidant of a couple. Comparing the three E^0 values, it is evident that

59 Pd^{II} and RCl are concurrent oxidants for Fe^0, Pd^{II} been the strongest. Therefore, if any RCl

60 removal enhancement is observed in the presence of Pd^{II} it is indirectly related to Fe^0

61 oxidation. Thus enhanced contaminant reduction by bimetallics [4,5,15] is an argument for

62 indirect reduction (by Fe^{II} or H/H_2 within the oxide film on Fe^0) [12]. Because of the

63 omnipresence of the oxide film, even if the reducing agent is H/H_2, the reduction is not likely

64 to occur at the Pd^0 surface. On the other hand Fe^{II} adsorbed onto the oxide film $(Fe^{II}_{(s)}$ or

65 structural Fe^{II}) has been shown to be a very strong reducing agent [16].

66 For illustration, consider an ideal redox indicator for the titration of Fe^0 by Pd^{II} (Eq. 1) having

67 a standard potential of 0.238 V. The redox half-reaction of the indicator is described by

68 equation 2 [17], where Ind_{ox} is the coloured oxidized form of the indicator, Ind_{red} is the

69 corresponding colourless reduced form, n is the number of electrons transferred (typically 1 or

70 2), and m is the number of protons transferred (typically 0, 1 or 2) and is dependent on the

71 pH.

72 $$Fe^0 + Pd^{2+} \Leftrightarrow Fe^{2+} + Pd^0 \qquad (1)$$

73 $$Ind_{ox} + ne^- + m\,H^+ \Leftrightarrow Ind_{red} \qquad (2)$$

74 $$Ind_{red} + Pd^{2+} \Leftrightarrow Ind_{ox} + Pd^0 \qquad (3)$$

75 The end of the titration (Fe^0 depletion) is detected by the appearance of a colour in the

76 solution. This colouration of the solution corresponds to the oxidation of the reduced form of

77 the indicator to the oxidized form (Eq. 3) by Pd^{2+} ions. To obtain accurate results, the lowest

78 possible amount of indicator should be used. In the titration context, no one can claim that

79 Pd^{II} enhances the reduction of Ind_{ox} by Fe^0. Pd^{II} oxidizes both Ind_{ox} and Fe^0. In this

80 competition Fe^0 is the stronger electron donor. Therefore, if any Ind_{ox} reduction enhancement

81 is observed in the presence of Pd^{II}, it can only indirectly be related to Fe^0 oxidation. It is true

82 that the surface of Pd^0 and not dissolved Pd^{II} is the catalyst for contaminant reduction by

83 H/H_2. The Pd^0 surface is however, shielded as a rule, and dissolved Pd^{II} will (at least partly)

84 co-precipitate with iron hydroxides and will no more be available for catalytic activity.

85 In conclusion, Pd^0 and other bimetallic elements (Co^0, Cu^0, Ni^0, Pt, Ru^0…) can not

86 significantly enhance contaminant reduction by elemental iron (electron from Fe^0 or from

87 H/H_2). Consequently, the reported increased contaminant removal by bimetallic systems is a

88 result of secondary redox processes within the oxide film on Fe^0 (electron from Fe^{II} or from

89 H/H_2). This conclusion is a further negation of the well-established concept of direct reductive

90 transformations as major decontamination process [9, 12].

91 For the further development of the iron reactive wall technology target experiments should be

92 performed to investigate the influence of hydrodynamic shear stress on the transport, transfer

93 and reaction rates within the oxide film, as well as film detachment under experimental

94 conditions pertinent to natural situations. This means that experiments must be performed

95 under conditions which favour oxide film formation and transformation. Redox processes

96 within a film on iron is well documented in the context of microbiologically influenced

97 corrosion [18].

101 **References**

102 [1] M. Haukka, M. Jakonen, T. Nivajärvi, M. Kallinen, The subtle effects of iron-containing

103 metal surfaces on the reductive carbonylation of $RuCl_3$. Dalton Trans. 26 (2006), 3212–3220.

104   [2] A.N. Nesmeyanov, R.Kh. Freidlina, E.C. Chukovskaya, R.G. Petrova, A.B. Belyavsky,

105   Addition, substitution, and telomerization reactions of olefins in the presence of metal

106   carbonyls or colloidal iron. Tetrahedron 17 (1962), 61–68.

107   [3] L.J. Matheson, P.G. Tratnyek, Reductive dehalogenation of chlorinated methanes by iron

108   metal. Environ. Sci. Technol. 28 (1994), 2045–2053.

109   [4] C.J. Lin, S.L. Lo, Y.H. Liou, Dechlorination of trichloroethylene in aqueous solution by

110   noble metal-modified iron. J. Hazard. Mater. 116 (2004), 219–228.

111   [5] R. Muftikian, Q. Fernando, N. Korte, A method for the rapid dechlorination of low

112   molecular weight chlorinated hydrocarbons in water. Water Res. 29 (1995), 2434–2439.

113   [6] G.E. Brown Jr., V.E. Henrich, W.H. Casey, D.L. Clark, C. Eggleston, A. Felmy, D.W.

114   Goodman, M. Grätzel, G. Maciel, M.I. McCarthy, K.H. Nealson, D.A. Sverjensky, M.F.

115   Toney, J.M. Zachara, Metal oxide surfaces and their interactions with aqueous solutions and

116   microbial organisms. Chem. Rev. 99 (1999), 77–174.

117   [7] S. Rakshit, C.J. Matocha, G.R. Haszler, Nitrate reduction in the presence of wüstite. J.

118   Environ. Qual. 34 (2005), 1286–1292.

119   [8] P. Schmuki, From Bacon to barriers: a review on the passivity of metals and alloys. J.

120   Solid State Electrochem. 6 (2002), 145–164.

121   [9] C. Noubactep, Processes of contaminant removal in "Fe^0-H$_2$O" systems revisited. The

122   importance of co-precipitation. Open Environ. J. 1 (2007), 9–13.

123   [10] E.J. Weber, Iron-mediated reductive transformations: investigation of reaction

124   mechanism. Environ. Sci. Technol. 30 (1996), 716–719.

125   [11] Y. Liu, F.L. Yang, P.L. Yue, G. Chen, Dechlorination of Chlorophenols by

126   Palladium/Iron. Water Res. 35 (2001), 1887–1890.

127   [12] C. Noubactep, A critical review on the mechanism of contaminant removal in Fe^0-H$_2$O

128   systems. Environ. Technol. 29 (2008), 909–920.

129 [13] C.G. Schreier, M. Reinhard, Catalytic hydrodehalogenation of chlorinated ethylenes

130 using palladium and hydrogen for the treatment of contaminated water. Chemosphere 31

131 (1995), 3475–3487.

132 [14] A.L. Roberts, L.A. Totten, W.A. Arnold, D.R. Burris, T.J. Campbell, Reductive

133 elimination of chlorinated ethylenes by zero-valent metals. Environ. Sci. Technol. 30 (1996),

134 2654–2659.

135 [15] D.M. Cwiertny, S.T. Bransfield, A.L. Roberts, Influence of oxidizing species on the

136 reactivity of iron-based bimetallic reductants. Environ. Sci. Technol. 41 (2007), 3734–3740.

137 [16] A.F. White, M.L. Peterson, Reduction of aqueous transition metal species on the surfaces

138 of Fe(II)-containing oxides. Geochimica et Cosmochimica Acta 60 (1996), 3799–3814.

139 [17] B.D. Jones, J.D. Ingle, Evaluation of redox indicators for determining sulfate-reducing

140 and dechlorinating conditions. Water Res. 39 (2005), 4343–4354.

141 [18] B. Little, P. Wagner, F. Mansfeld, An overview of microbiologically influenced

142 corrosion. Electrochim. Acta 37 (1992), 2185–2194.