1   **Comments on "Reduction of chromate by granular iron in the presence of dissolved**

2   **CaCO$_3$" by Gui et al. [Appl. Geochem. 24 (2009) 677–686]**

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7   In a recent study, Gui et al. (2009) conducted column experiments to determine the effects of

8   dissolved CaCO$_3$ on the reactivity of metallic iron (Fe^0) towards Cr^{VI} reduction and hydraulic

9   conductivity. For their discussion, the authors considered Cr^{VI} reduction by Fe^0 as a surface-

10   mediated process. The thermodynamic instability of Fe^0 in water favours the oxidation of Fe^0

11   to Fe^{II}/Fe^{III} species and the precipitation of iron species on the Fe^0 surface (oxide film or

12   oxide layer). The oxide film will severely impede the electron transfer from Fe^0 to Cr^{VI},

13   decreasing the transformation rate of Cr^{VI} to Cr^{III}. On the other hand, in situ generated solid

14   iron species will certainly reduce the permeability of the Fe^0 wall (loss of hydraulic

15   conductivity). The consideration of Gui et al. (2009) is in conformity with the state-of-the-art

16   knowledge on the mechanism of reducible contaminants in the presence of Fe^0 (e.g. in

17   Fe^0/H$_2$O systems). However, there are strong evidences that "Cr^{VI} reduction at the surface of

18   Fe^{0}" may not be consistent.

19   First, quantitative Cr^{VI} reduction to Cr^{III} by (i) Fe^{II}-bearing commercial chemical reductants,

20   e.g. FeSO$_4$.7H$_2$O (Park et al., 2008), (ii) various Fe^{II}-bearing natural minerals including green

21   rusts (Eary and Rai, 1988; White and Peterson, 1996), and (iii) electrically generated Fe^{II}

22   (Zongo et al., 2009) has been reported. These reports suggest that Cr^{VI} may be reduced in the

23   aqueous phase by Fe^{II} from Fe^0 oxidation (primary corrosion products). Cr^{VI} may also be

24   reduced within the oxide film on Fe^0 by green rusts which are always available in (anoxic)

25   Fe^0/H$_2$O systems (Chaves, 2005). Therefore, considering Cr^{VI} reduction to Cr^{III} in a Fe^0/H$_2$O

26   system a priori as a surface-mediated process may not be acceptable. Moreover, it is not

27   certain whether the Fe^0 surface do play any direct role in the process of Cr^{VI} reduction, since

28   diffusion of Cr^{VI} to Fe^0 is necessarily the rate-determining step.

29   Second, Cr^{VI} reduction to Cr^{III} by Fe^{II} adsorbed at the surface of minerals (so called structural

30   Fe^{II}) has been reported (Fendorf and Li, 1996; White and Peterson, 1996). In particular, White

31   and Peterson (1996) reported that the electrode potential for the redox couple $Fe^{III}(s)/Fe^{II}(s)$

32   ranges from -0.34 to -0.65 V. This makes structural Fe^{II} a stronger reducing agent than Fe^0

33   (table 1) under some circumstances (E < -0.44 V). Clearly, Cr^{VI} reduction to Cr^{III} can be

34   mediated by metallic iron (Fe^0), structural Fe^{II}, molecular H_2, and dissolved Fe^{II}. Given that at

35   pH value > 5 the Fe^0 surface is always shielded by an oxide film, there is no reason for

36   quantitative Cr^{VI} reduction at the Fe^0 surface.

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38   **Table 1**: Relevant half-reactions for the discussion of the mechanism of Cr^{VI} removal in

39   Fe^0/H_2O systems and their relevant standard reduction potentials (E^0). E^0 values

40   are arranged in increasing order. The lower the E° value, the stronger the reducing

41   capacity for Cr^{VI} (e.g. CrO_4^{2-}). All reducing agents (Fe^0, $Fe^{II}_{(s)}$, $H_{2(g)}$ and $Fe^{II}_{(aq)}$)

42   can reduce CrO_4^{2-} to Cr^{3+}.

Equation	Half-reaction	E^0(V)
(1)	$Fe^{2+} + 2e^- \Leftrightarrow Fe^0$	-0.44
(2)	$Fe^{3+}_{(s)} + e^- \Leftrightarrow Fe^{2+}_{(s)}$	-0.34 to -0.65
(3)	$2\,H^+_{(aq)} + 2\,e^- \Leftrightarrow H_{2(g)}$	0.00
(4)	$Fe^{3+}_{(aq)} + e^- \Leftrightarrow Fe^{2+}_{(aq)}$	0.77
(5)	$CrO_4^{2-} + 8\,H^+ + 3e^- \Leftrightarrow Cr^{3+} + 4\,H_2O$	1.51

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44   Third, a Fe^0 bed can be considered as filter removing Cr^{VI} by simple size exclusion processes.

45   Since the in situ generated iron oxides occupy the pore spaces (loss of hydraulic conductivity)

46   they do increase the filtration capacity/efficiency. Therefore, with increasing service life a Fe^0

47   bed may remove Cr^{VI} without any chemical transformation nor strong adsorptive interactions.

48   The superiority of Fe^0 versus Fe^{II}-bearing materials for the reductive precipitation of Cr^{IV} is

49   well documented (Gould, 1982; Park et al., 2008; Gui et al., 2009). The theoretical facts

50   above demonstrate this is because of the continuous production of reactive Fe^{II} ($Fe^{II}_{(aq)}$ and

51     $Fe^{II}_{(s)}$) and the diversity of reducing agents in the Fe^0/H_2O system (Gould, 1982). Therefore,

52   Fe^0 could be considered as a source for the in-situ production of oxide film and reducing

53   agents for Cr^{VI} removal (Noubactep, 2007; Noubactep, 2008). Clearly, Cr^{IV} reduction mostly

54   occurs within the oxide film. This conclusion corroborates the results of iron

55   electrocoagulation. In fact, Cr^{VI} removal in electrocoagulation using iron electrodes (Fe^0 EC)

56   was shown to occur as follows: (i) Cr^{VI} is reduced by electrochemically generated Fe^{II} species

57   (yielding Cr^{VI} and Fe^{III}), (ii) resulted Cr^{III} is coagulated by freshly formed Fe^{III} agent. The

58   efficiency of Fe^0 EC relies on both the reduction of Cr^{VI} and the promoted oxidation of Fe^{II}

59   (Zongo et al., 2009). Fe^0 EC should be considered as an electrochemically driven accelerated

60   corrosion process. Therefore, the processes are rigorously the same with the sole and subtle

61   difference that corrosion is electrically accelerated in Fe^0 EC.

62   Cr^{VI} removal in column studies (and Fe^0 field reactive barriers) combines the size exclusion

63   effect of the Fe^0 bed and the chemical reactivity of Fe^0. Because adsorbents are in situ

64   generated and transformed (aged), iron oxides of various adsorbing capacity are certainly

65   available in any Fe^0/H_2O system and are good adsorbents for Cr^{VI} (and Cr^{III}). Oxide films

66   continually grow into the metal at the Fe^0/film interface while being simultaneously

67   restructured at the film/H_2O interface. Accordingly, at the interface Fe^0/film, a continual

68   generation and annihilation of point defects occurs and this interface can be considered as

69   "living" (Sikora and Macdonald, 2000). Aged iron oxides at the film/H_2O interface should be

70   regarded as "dead" or simple "coatings" with limited Cr^{VI} adsorption capacity. However, it is

71   not likely that inflowing Cr^{VI}, which is first adsorbed onto "dead" oxides will readily further

72   migrate to the "living" layer which is necessarily richer in Fe^{II} species in order to be reduced

73   to Cr^{III}. Therefore, despite spectroscopic evidences of Cr^{III} in Fe^0/H_2O systems (e.g. Raman

74   spectra), Cr^{VI} reduction may not be quantitative in the long term. A time scale investigation of

75   Cr mass balance accompanied by a speciation of total Cr is necessary to addressed this

76   important issue.

77   In conclusion, a close analysis of the Fe^0/H_2O system shows in agreement with

78   electrocoagulation using iron electrodes that Fe^0 is a source of reactive species (oxide film,

79   molecular hydrogen and Fe^{II} species) for Cr^{VI} adsorptive or reductive removal. Although the

80   reductive removal may be quantitative, its long-term effectiveness should be closely

81   investigated. In the light of the discussion above, the influence of $CaCO_3$ on the process of

82   Cr^{VI} removal in Fe^0/H_2O systems should be reconsidered. It seems that the major question to

83   answer in this effort is: what is the impact of $CaCO_3$ on the formation and transformation of

84   oxide film on Fe^0? To this end, a third column without Cr^{VI} inflow could serve as reference

85   system to evidence the impact of Cr^{VI} on Fe^0 corrosion as measure by decrease of hydraulic

86   conductivity. Whether removed Cr is chemically transformed nor not, the most important

87   issue is its long-term stability within the Fe^0/H_2O system.

88   **References**

89   Chaves, L.H.G., 2005. The role of green rust in the environment: a review. Rev. Bras. Eng.

90   Agríc. Ambient.9, 284–288.

91   Eary, L.E., Rai, D., 1988. Chromate removal from aqueous wastes by reduction with ferrous

92   ion. Environ. Sci. Technol. 22, 972–977.

93   Fendorf, S.E., Li, G. 1996. Kinetics of chromate reduction by ferrous iron. Environ. Sci.

94   Technol. 30, 1614–1617.

95   Gould, J.P, 1982. The kinetics of hexavalent chromium reduction by metallic iron. Water Res.

96   16, 871–877.

97 Gui, L., Yang, Y., Jeen, S.-W., Gillham, R.W., Blowes, D.W., 2009. Reduction of chromate

98 by granular iron in the presence of dissolved $CaCO_3$. Appl. Geochem. 24, 677–686.

99 Noubactep, C., 2007. Processes of contaminant removal in "Fe^0–H_2O" systems revisited. The

100 importance of co-precipitation. Open Environ. J. 1, 9–13.

101 Noubactep, C., 2008. A critical review on the mechanism of contaminant removal in Fe^0–H_2O

102 systems. Environ. Technol. 29, 909–920.

103 Park, D., Lim, S.-R., Lee, H.W., Park, J.M., 2008. Mechanism and kinetics of Cr(VI)

104 reduction by waste slag generated from iron making industry. Hydrometallurgy 93, 72–75.

105 Sikora, E., Macdonald, D.D., 2000. The passivity of iron in the presence of

106 ethylenediaminetetraacetic acid I. General electrochemical behavior. J. Electrochem. Soc.

107 147, 4087–4092.

108 White, A.F., Peterson, M.L., 1996. Reduction of aqueous transition metal species on the

109 surfaces of Fe(II)-containing oxides. Geochim. Cosmochim. Acta 60, 3799–3814.

110 Zongo, I., Leclerc, J.-P., Maïga, H.A., Wéthé, J., Lapicque, F., 2009. Removal of hexavalent

111 chromium from industrial wastewater by electrocoagulation: A comprehensive comparison of

112 aluminium and iron electrodes. Sep. Purif. Technol. 66, 159–166.