1   Comments on: "**Decontamination of solutions containing EDTA using metallic iron**" By

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8   **Abstract**

9   This letter presents an improved discussion of the data provided in a recent article on EDTA

10   removal from aqueous solutions using elemental iron (Fe^0) by O. Gyliene and his co-workers.

11   It is shown that the authors have furnished a brilliant validation of the concept that dissolved

12   contaminants are primary removed in Fe^0/H_2O systems by adsorption onto iron corrosion

13   products and co-precipitation with iron corrosion products. It is reiterated that "contaminant

14   removal" and "contaminant reduction" should not be interchanged randomly.

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18   In a recent article entitled "Decontamination of solutions containing EDTA using metallic

19   iron" O. Gyliene and his coworkers [1] discussed the effects of initial pH value, EDTA

20   concentration, Fe^0 dosage, Cu^{II} addition, and molecular oxygen (access of air) on the removal

21   of Ethylenediaminetetraacetate (EDTA) by Fe^0. Pure iron powder and plates of carbon steel

22   were use as Fe^0 source. The used EDTA concentrations were 1, 10 and 100 mmol/L; the used

23   Cu^{II} concentrations were 0 and 10 mmol/L; and the tested initial pH values varied from 3 to 7.

24   The solutions were vigorously mixed with a magnetic stirrer and the equilibration time varied

25   from a few hours to several days. The results showed that "EDTA decomposition" is

26   significantly enhanced in the presence of Cu^{II} and molecular oxygen. Furthermore, EDTA and

27   its reaction products ("degradation products") co-precipitated with corrosion products as

28   identified by FT-IR spectroscopy.

29   The study of Gyliene et al. [1] is very informative to researchers interested in the field of iron

30   technology. However, the article contains areas where improvements could be made that will

31   be discussed below.

32   **State of the art on the Fe^0-EDTA-H_2O system**

33   The originality of the study of Gyliene et al. [1] is that EDTA is the contaminant to be

34   removed. In investigating contaminant reduction by Fe^0, previous studies have used EDTA as

35   chelating agent to sustain iron dissolution and avoid precipitation of corrosion products on the

36   Fe^0 surface [2-4]. Alternatively, EDTA was used to characterize the forward dissolution of

37   Fe^0 materials and therefore characterize their reactivity in a contaminant free system [5,6].

38   From the perspective of rendering Fe^0 accessible by adding EDTA, the effect of Cu^{II} addition

39   as discussed by Gyliene et al. [1] can be improved. In fact, Cu^{II} removal by Fe^0 is a very well-

40   documented metallurgical process [7], that has also been reported in the context of

41   remediation by Fe^0 [8]. Accordingly, EDTA keeps Fe^0 surface free for Cu^{II} reduction

42   (cementation). The chemical reaction involved in the cementation of copper species by Fe^0 is

43   represented by the following redox reaction:

44      $$Fe^0 + Cu^{2+} \Rightarrow Fe^{2+} + Cu^0 \qquad\qquad (1)$$
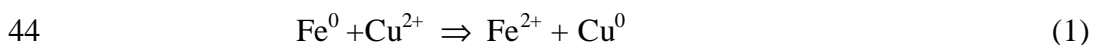
45   During this reaction, elemental copper (Cu^0) is deposited at cationic sites on Fe^0 surface while

46   dissolution of iron (Fe^{2+} release) takes place at anionic sites [9]. When the surface of iron is

47   covered by an oxide film the fate of Cu^{II} that has been removed from the aqueous phase is

48   unclear. For example, the mechanism for Cu^{II} removal may occur via (i) adsorption onto the

49   oxide-film or underlying Fe^0 surface, (ii) co-precipitation with newly generated iron

50   hydroxides, (iii) direct reduction by Fe^0, and (4) indirect reduction by Fe^{II}, green rust, or H/H_2

51   redox couple. Reduction reactions may take place at the Fe^0 surface or within the oxide film.

52   Therefore, equations similar to Eq. 1 which are usually written to explain the removal process

53 of reducible contaminants in Fe^0/H_2O systems does not fully explain the complexity involved

54 in removal. For example, non reducible aqueous contaminants such as triazoles [10] and zinc

55 [11] as well as viruses [12] have been successfully removed from solution by Fe^0. To explain

56 the contaminant removal efficiency of Fe^0/H_2O systems, a new concept (next section) was

57 introduced that considers adsorption and co-precipitation as the primary contaminant removal

58 mechanisms [13,14]. The data discussed in the manuscript by Gyliene et al. [1] provide

59 additional support for the afore mentioned concept.

60 **The adsorption/co-precipitation concept**

61 The mechanism of aqueous contaminant removal in Fe^0/H_2O systems has been largely

62 discussed in the literature [4,10,15]. Two major removal mechanisms are usually discussed:

63 (i) contaminant adsorption onto Fe^0 oxidation products, and (ii) contaminant reduction by Fe^0,

64 Fe^{II} or H/H_2. Re-evaluating a seminal work of Matheson and Tratnyek [4], Weber [15]

65 proposed the currently widely accepted concept for contaminant removal: "the reductive

66 transformation concept". This concept implicitly considered Fe^0 as reducing agent (direct

67 reduction) and reduction as "a surface-mediated process. A closer inspection of the chemistry

68 of the Fe^0/H_2O system revealed that adsorption and co-precipitation are the fundamental

69 removal mechanisms [13,14]. It was demonstrated that the concept of contaminant reductive

70 transformation [4,15] does not take into account that corrosion product generation is a

71 dynamic process in the course of which contaminants are entrapped in the matrix of iron

72 hydroxides. However, contaminant co-precipitation with iron hydroxides/oxides is a well-

73 documented unspecific removal mechanism [16-18]. Contaminant co-precipitation as primary

74 removal mechanism is compatible with subsequent reduction.

75 **EDTA removal by Fe^0 validates the adsorption/co-precipitation concept**

76 In open systems, Gyliene et al. [1] have induced EDTA degradation by oxygen activation in a

77 Fe^0/air/water system [19-21]. The most important results from Gyliene et al. [1] are threefold:

78 (i) Cu^{II} is readily removed from the aqueous phase by cementation (eq. 1), (ii) Cu^{II} enhances

79 EDTA removal and (iii) there is some delay in the process of EDTA removal by Fe^0. The fact

80 that Cu^{II} removal was completed two hours after the start of the experiment while quantitative

81 EDTA removal started only after three hours eliminates catalytic activity as possible

82 enhancement mechanism for EDTA removal. Only the second argument of Gyliene et al. [1]

83 might be significant: "The reason of enhancing effect of Cu^{II} ions on decontamination could

84 be also the increased corrosion rate of iron in solutions of Cu^{II} ions". The only way for

85 accelerated iron corrosion to enhance EDTA removal with a lag time goes through

86 transformations of primary corrosion products (Fe^{II}) occurring with a time delay. Primary

87 corrosion products (Fe^{II}) are transformed into Fe^{III} and Fe^{II}/Fe^{III} species which precipitate

88 upon saturation. The oxidation of $Fe^{II}EDTA$ to $Fe^{III}EDTA$ is a very rapid process [22,23]. The

89 presence of EDTA delay iron hydroxides (and oxyhydroxides) precipitation [2-6] and EDTA

90 quantitative removal starts with the depletion of the chelating capacity of EDTA

91 (consumption of available amount) [6]. During the precipitation process, EDTA and its

92 reaction (oxidation or degradation) products are entrapped in the matrix of iron hydroxides as

93 evidenced by FT-IR spectroscopy. Therefore, the results of Gyliene et al. [1] can be seen as

94 the validation of the concept of contaminant adsorption/co-precipitation as fundamental

95 mechanisms of contaminant removal in Fe^0/H_2O systems [13].

96 **Conclusions**

97 The discussion above unequivocally show that the results of Gyliene et al. [1] are better

98 interpreted by the adsorption/co-precipitation concept [13]. Furthermore it is shown that

99 "contaminant removal", "contaminant degradation" and "contaminant reduction" should not

100 be interchanged randomly. A removed contaminant can be further reduced/oxidized and a

101 reduced/oxidized contaminant can be further removed. The latter aspect is excellently

102 documented by Gyliene et al. [1] who clearly showed that oxidized EDTA is removed by co-

103 precipitation. These results suggest that the debate between β-elimination or hydrogenolysis

104 as the main dechlorination mechanism for chlorinated ethylenes should be revisited [24,25].

105 In fact, if chlorinated ethylenes and their reaction products co-precipitated with corrosion

106 products, the discussion on the toxicity of daughter products should be reconsidered.

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