

1 **Comments on “pH Dependence of Fenton Reagent Generation and As^{III} Oxidation and**
2 **Removal by Corrosion of Zero Valent Iron in Aerated Water”**

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7 Katsoyiannis et al. (1) discussed the kinetics and mechanism of As^{III} oxidation and removal
8 by elemental iron (Fe⁰) in aerated waters as function of the pH value and concluded that As^{III}
9 is oxidized in the aqueous phase by the Fenton reaction and removed by sorption on newly
10 formed hydrous ferric oxides. This paper attempted to elucidate the mechanism of arsenic
11 (As) removal in Fe⁰/H₂O systems as used worldwide in permeable reactive barriers (2) and in
12 Fe⁰ filters (3). In this regard, it should be recalled that the SONO filters contain “a specially
13 manufactured composite iron matrix” (4) and are not pure Fe⁰/H₂O systems. Fe⁰ was used in a
14 previous step of SONO filter development. The discussion on the mechanism of As^{III} removal
15 given by Katsoyiannis et al. (1) could be improved.

16 **The process of iron precipitation: Arsenic removal by corrosion products**

17 If under the experimental conditions of Katsoyiannis et al. (1) only 1 % of used Fe⁰ dissolves,
18 this will result to an iron concentration of 150 µg/L Fe (27 µM). At pH 5 for example 99.6 %
19 of dissolved Fe will precipitated before a stable solution is obtained (0.56 µg/L – ref. 5).

20 In a system of precipitating iron hydroxides, As^{III} can be removed from the aqueous phase by
21 adsorption and co-precipitation. The distinction between adsorption and co-precipitation is
22 not always clear. Dissolved species adsorb onto existing solid substrates as a rule. Co-
23 precipitation occurs when the solid substrate is formed in the presence of dissolved species to
24 be removed from solution (6). In experiments targeted at removing arsenite and arsenate from
25 aqueous solution by ferrihydrite, similar sorption densities have been reported for arsenite
26 adsorption and co-precipitation with ferrihydrite whereas significantly greater sorption

27 densities have been found for arsenate co-precipitated with ferrihydrite (molar ratio Fe:As =
28 1.4) as compared to post-synthesis adsorption (molar ratio Fe:As = 4.0) (7).

29 The presentation above shows that an over-saturated iron solution emerges from the
30 dissolution of 1% of Fe⁰ used by Katsoyiannis et al. (1). The over-saturation at pH 5.0 (96.6
31 %) corresponds to 26.7 μM of Fe that may spontaneously precipitate in the presence of only
32 2.0 μM of As. The resulting molar ratio Fe:As (> 12) suggests that As^{III} co-precipitation with
33 excess dissolved Fe or As^{III} adsorption onto ferrihydrite might be the major pathway of As
34 removal from the aqueous phase (8).

35 **Did As^{III} removal precedes oxidation?**

36 In considering that As^{III} is oxidized in the aqueous phase to As^V which is subsequently
37 removed by sorption on newly formed hydrous ferric oxides, Katsoyiannis et al. (1) have not
38 properly considered the dynamic of iron oxide precipitation (8). The effects of newly formed
39 hydrous ferric oxides on As^{III} may be summarized in two hypotheses. First, As^{III} is oxidized
40 in the aqueous phase (Assumption 1). Second, As^{III} is oxidized in the solid phase (Assumption
41 2). The validity of Assumptions 1 and 2 will be discussed on the basis of an analysis of the
42 evolution of the Fe⁰/H₂O system.

43 The above calculations for 1 % Fe consumption show that arsenic (As^{III} and As^V) may be
44 entrapped in the matrix of precipitating iron oxides (co-precipitation). This statement is valid
45 irrespective from the presence of any oxidizing agent. Therefore, there is no reason why in the
46 presence of oxidizing agents As^{III} should first oxidize to As^V before been adsorbed onto iron
47 hydroxides. As^{III} and As^V species certainly have different affinity to iron hydroxides but co-
48 precipitation as discussed here is primarily a non-specific process. Thus, there is no reason
49 why assumption 1 should be valid as a rule.

50 The lag time reported by Katsoyiannis et al. (1) can be regarded as the time necessary for the
51 production of reactive species (iron hydroxides, radicals, H₂O₂). This lag time has no practical
52 significance for field installations because an aqueous contaminant flowing into an engineered

53 Fe⁰/H₂O system enters a domain of precipitating iron hydroxides. The contaminant is just a
54 foreign specie which can be more or less strongly adsorbed by already available reactive
55 species or co-precipitate with forming iron hydroxides. The adsorptive reactivity of available
56 species is known to depend on several factors including, their age, their crystallinity, and their
57 porosity. It is certain than an As^{III} species adsorbed in the pores of iron hydroxides can be
58 oxidized at their location by dissolved oxidizing agents (including radicals and H₂O₂).
59 Therefore, Assumption 2 is more likely to be universally valid.

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