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

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Katsoyiannis et al. (1) discussed the kinetics and mechanism of As\textsuperscript{III} oxidation and removal by elemental iron (Fe\textsuperscript{0}) in aerated waters as function of the pH value and concluded that As\textsuperscript{III} is oxidized in the aqueous phase by the Fenton reaction and removed by sorption on newly formed hydrous ferric oxides. This paper attempted to elucidate the mechanism of arsenic (As) removal in Fe\textsuperscript{0}/H\textsubscript{2}O systems as used worldwide in permeable reactive barriers (2) and in Fe\textsuperscript{0} filters (3). In this regard, it should be recalled that the SONO filters contain “a specially manufactured composite iron matrix” (4) and are not pure Fe\textsuperscript{0}/H\textsubscript{2}O systems. Fe\textsuperscript{0} was used in a previous step of SONO filter development. The discussion on the mechanism of As\textsuperscript{III} removal given by Katsoyiannis et al. (1) could be improved.

The process of iron precipitation: Arsenic removal by corrosion products

If under the experimental conditions of Katsoyiannis et al. (1) only 1 % of used Fe\textsuperscript{0} dissolves, this will result to an iron concentration of 150 µg/L Fe (27 µM). At pH 5 for example 99.6 % of dissolved Fe will precipitated before a stable solution is obtained (0.56 µg/L – ref. 5).

In a system of precipitating iron hydroxides, As\textsuperscript{III} can be removed from the aqueous phase by adsorption and co-precipitation. The distinction between adsorption and co-precipitation is not always clear. Dissolved species adsorb onto existing solid substrates as a rule. Co-precipitation occurs when the solid substrate is formed in the presence of dissolved species to be removed from solution (6). In experiments targeted at removing arsenite and arsenate from aqueous solution by ferrihydrite, similar sorption densities have been reported for arsenite adsorption and co-precipitation with ferrihydrite whereas significantly greater sorption
densities have been found for arsenate co-precipitated with ferrihydrite (molar ratio Fe:As = 1.4) as compared to post-synthesis adsorption (molar ratio Fe:As = 4.0) (7).

The presentation above shows that an over-saturated iron solution emerges from the dissolution of 1% of Fe\textsuperscript{0} used by Katsoyiannis et al. (1). The over-saturation at pH 5.0 (96.6 \%) corresponds to 26.7 µM of Fe that may spontaneously precipitate in the presence of only 2.0 µM of As. The resulting molar ratio Fe:As (> 12) suggests that As\textsuperscript{III} co-precipitation with excess dissolved Fe or As\textsuperscript{III} adsorption onto ferrihydrite might be the major pathway of As removal from the aqueous phase (8).

Did As\textsuperscript{III} removal precedes oxidation?

In considering that As\textsuperscript{III} is oxidized in the aqueous phase to As\textsuperscript{V} which is subsequently removed by sorption on newly formed hydrous ferric oxides, Katsoyiannis et al. (1) have not properly considered the dynamic of iron oxide precipitation (8). The effects of newly formed hydrous ferric oxides on As\textsuperscript{III} may be summarized in two hypotheses. First, As\textsuperscript{III} is oxidized in the aqueous phase (Assumption 1). Second, As\textsuperscript{III} is oxidized in the solid phase (Assumption 2). The validity of Assumptions 1 and 2 will be discussed on the basis of an analysis of the evolution of the Fe\textsuperscript{0}/H\textsubscript{2}O system.

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

The lag time reported by Katsoyiannis et al. (1) can be regarded as the time necessary for the production of reactive species (iron hydroxides, radicals, H\textsubscript{2}O\textsubscript{2}). This lag time has no practical significance for field installations because an aqueous contaminant flowing into an engineered
Fe\textsuperscript{0}/H\textsubscript{2}O system enters a domain of precipitating iron hydroxides. The contaminant is just a foreign specie which can be more or less strongly adsorbed by already available reactive species or co-precipitate with forming iron hydroxides. The adsorptive reactivity of available species is known to depend on several factors including, their age, their crystallinity, and their porosity. It is certain than an As\textsuperscript{III} species adsorbed in the pores of iron hydroxides can be oxidized at their location by dissolved oxidizing agents (including radicals and H\textsubscript{2}O\textsubscript{2}). Therefore, Assumption 2 is more likely to be universally valid.

**Literature Cited**


