

1 **Comments on “Stoichiometry of Cr^{VI} immobilization using nanoscale zerovalent iron**
2 **(nZVI): A study with High-Resolution X-Ray Photoelectron Spectroscopy (HR-XPS).”**
3 **by Li et al. [Ind. Eng. Chem. Res. 47, 2131–2139].**

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8 Sir: Li et al.¹ have collected valuable data on the process of Cr^{VI} removal in Fe⁰/H₂O systems.
9 They evaluated Cr^{VI} reductive precipitation by nanoscale zerovalent iron (nZVI) using High-
10 Resolution X-Ray Photoelectron Spectroscopy and concluded that, nZVI “mainly acts as a
11 reductant” for Cr^{VI} removal. The study of Li et al.¹ is very informative to researchers
12 interested in the field of iron technology. However, the given discussion should be regarded
13 as a further propagation of a misconception for two major reasons.

14 First: irrespective from the size of used Fe⁰-material (nm, μm, mm), any Fe⁰/H₂O system is a
15 system generating Fe^{II} and Fe^{III} species. Depending from the solution chemistry, both species
16 may precipitate. In the course of precipitation, available foreign species will be entrapped in
17 their structure (co-precipitation). Contaminant co-precipitation should be primarily regarded
18 as a non-specific process. The relative proportion of foreign species in the co-precipitates
19 depends on: (i) the contaminant initial concentration, (ii) the initial Fe⁰ loading, and (iii) the
20 reactivity of used Fe⁰. If the contaminant is a metal (e.g. Cr) initially present at concentrations
21 above the solubility limit (up to 2000 mg/L or 38.5 mM in ref. 1 – see ref. 2 for Cr^{III} solubility
22 limit), the initial stage of the reaction will be characterised by the precipitation of
23 contaminant, iron been co-precipitated as the foreign species. Using over-saturated metal
24 concentrations is not justified because (i) over-saturation is rare in nature and (ii) in real world
25 systems, Fe⁰ is covered by a more or less thick layer of corrosion products (oxide-film) before
26 contaminant inflow occurs. Because Li et al.¹ have not properly addressed these points the

27 relevance of their discussion for practical systems is yet to be demonstrated. In particular
28 there is no reason why Cr^{VI} should be reduced to Cr^{III} before precipitation. It should be
29 recalled that aqueous reduction of Cr^{VI} by dissolved Fe^{II} is favourable. On the other hand, co-
30 precipitated Cr^{VI} can be further reduced and adsorbed Fe^{II} is a stronger reductant than
31 dissolved Fe^{II} .³ A more coherent approach considering contaminant adsorption onto and/or
32 contaminant co-precipitation with iron corrosion products as fundamental mechanism of
33 contaminant removal in $\text{Fe}^0/\text{H}_2\text{O}$ system has recently been introduced^{4,5} and is currently
34 discussed in the literature.^{6,7}

35 Second: Li et al.¹ have shaken their reaction bottles at an intensity as high as 300 rpm. This
36 operation has been proven disturbing for investigations of natural relevance^{4,5,8}. In fact, under
37 such strong mixing regimes the formation of the oxide-film on Fe^0 is disturbed (delayed or
38 avoided). However, the aqueous reactivity of any metal (M^0) is determined in large part by
39 the transport properties of the corrosion product layer (oxide-film) at its surface. Both ionic
40 and electronic transport are important. The reactive metal substrate (M^0) is seldom, if ever, in
41 direct contact with the electrolyte; instead, an oxide-film separates the metal and the aqueous
42 phase. If the oxide-film is a barrier to transport (e.g. oxide-film on Al^0), the corrosion rate is
43 low and the metal is categorized as passive under the exposure conditions. If the oxide-film is
44 not a barrier (e.g. oxide-film on Fe^0), corrosion proceeds.⁹ Therefore, for continued corrosion,
45 an oxide-film capable of high ionic transport is required at the M^0 surface. The electronic
46 transport properties will affect the spatial distribution of reduction reactions in the corroding
47 system. With sufficient electronic conductivity, reduction reactions can proceed at the outer
48 surface of the oxide-film, i.e. the corrosion product can act as an electrode for electrochemical
49 reactions.⁹ However, for Fe^0 this electrochemical reaction path competes with indirect
50 reduction through Fe^{II} which may be more favorable.^{4,5}

51 The discussion above demonstrated that the chemistry of the $\text{Fe}^0/\text{Cr}^{\text{VI}}/\text{H}_2\text{O}$ system was not
52 properly considered by Li et al.¹. The most important question for $\text{Fe}^0/\text{H}_2\text{O}$ systems for Cr^{VI}

53 removal is how long Cr^{VI} removal will be successful or what is the impact of Cr^{VI} on the ionic
54 and electronic transport properties of oxide-films on Fe⁰? Answering this question for
55 situations pertinent to natural systems is a challenge to the scientific community. In this effort
56 the use of ill-defined notion as “Fe⁰ removal capacity” should be avoided. Fe⁰ removal
57 efficiency depends on the reactivity of Fe⁰, the flux of contaminant, the water chemistry.

58 **Literature Cited**

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