

1 **Comment on “Coupled acidification and ultrasound with iron enhances**  
2 **nitrate reduction” by Tsai et al. J. Hazard. Mater. 163 (2009) 743**

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7 In a recent study, Tsai et al. [1] reported on their investigation of the effect of solution pH  
8 ( $H^+$ ) and ultrasound (US) on the destruction of passive oxide on metallic iron ( $Fe^0$ ). The aim  
9 of the study was to sustain  $Fe^0$  reactivity upon nitrate reductive degradation. Their results  
10 showed that ultrasound, used alone (US/ $H_2O$  system) or with  $Fe^0$  (US/ $Fe^0/H_2O$  system) could  
11 not induce nitrate ( $NO_3^-$ ) reductive degradation. Enhanced  $NO_3^-$  degradation could be  
12 observed at low pH values ( $Fe^0/H^+$  system) and the degradation was further enhanced by  
13 sonication (US/ $Fe^0/H^+$  system). Tsai et al. [1] concluded that US was helpful in destroying or  
14 preventing the formation of passive film on  $Fe^0$  in acidic solution. However, there is strong  
15 evidence that these conclusions are not supported by own experimental data.

16 First, the fact that no significant difference between the systems US/ $H_2O$  and US/ $Fe^0/H_2O$   
17 could be observed indicates that something was wrong in the experimental design. The  
18 reaction time ( $\leq 4$  h) was likely too short for the used US power (150 W) and frequency (43  
19 kHz). Enhancing the power and the frequency of US or lengthen the experimental duration  
20 (e.g.  $> 4$  h) would have certainly yield better results. A complementary  $Fe^0/H_2O$  system  
21 should have been investigated to limit speculations. Rigorously, Tsai et al. [1] have performed  
22 their experiments in undisturbed systems (very low mixing conditions). Powdered  $Fe^0$  was  
23 condensed at the bottom of the vials. Therefore,  $NO_3^-$  transport to  $Fe^0$  is influenced by gravity  
24 or US radiation. Obviously, the used power and the frequency of US radiation were too low to  
25 induce noticeable  $NO_3^-$  transport within 4 h. The combined effect of the mixing intensity and  
26 the reaction time were comprehensively discussed by Noubactep et al. [2].

27 Second, Tsai et al. [1] intended to “investigate the effects of ultrasound and pH on the  
28 destruction of passive oxide film”. However, they investigated at most the effects of  
29 ultrasound and pH in avoiding the formation of passive oxide films on  $\text{Fe}^0$ . In fact, in order to  
30 investigate the destruction of any film, one has to first favour its formation. For example by  
31 pre-equilibration  $\text{Fe}^0/\text{H}_2\text{O}$  systems at neutral pH value and then add acid or apply ultrasonic  
32 vibrations. At two of the three tested initial pH values (2 and 4) iron is readily soluble and  
33 oxide films will not formed immediately after the start of the experiments. Keeping the pH  
34 low will avoid the formation of the film.

35 Third, the increase in pH value is used to support degradation pathway while adsorption an  
36 co-precipitation are not mentioned [3, 4]. However, the results of Tsai et al. [1] showed  
37 clearly that  $\text{Fe}^0$  oxidation was not mediated by  $\text{NO}_3^-$ . In fact, when the initial pH was 2.0, the  
38 final pH values varied from 3.42 to 3.83. This corresponds to a protons consumption ( $[\text{H}^+] =$   
39  $10^{-\text{pH}}$ ) of about 390  $\mu\text{moles}$  in 40 mL solution. The initial concentration of  $\text{NO}_3^-$  (100 mg/L)  
40 corresponds to 65  $\mu\text{moles}$  of  $\text{NO}_3^-$  in 40 mL solution. The resulting molar ratio  $\text{H}^+/\text{NO}_3^-$  of 6  
41 suggest in agreement with well documented results from the corrosion science, that  $\text{Fe}^0$  is  
42 oxidized by acidic dissolution [5]. Moreover this large molar ratio indicate that enough iron  
43 oxides was generated in the system to co-precipitate possibly reduced  $\text{NO}_3^-$ . Here, removed  
44  $\text{NO}_3^-$  is not necessarily reduced and reduced  $\text{NO}_3^-$  is not necessarily transformed by electrons  
45 from  $\text{Fe}^0$  (direct reduction) [3, 4].

46 Fourth, the statement that “minor changes in pH indicate that the chemical reduction process  
47 by  $\text{Fe}^0$  did not progress significantly” contradicts well-documented results from the iron  
48 corrosion. In fact, oxygen reduction is the major cathodic reaction during the immersed and  
49 atmospheric  $\text{Fe}^0$  corrosion of iron for pH values  $> 4$ . For example, Stratmann and Mueller [6]  
50 analysed the relation between the kinetics of the  $\text{O}_2$  reduction and the reduction of the oxide  
51 film. Their results showed that oxygen is predominantly reduced (by  $\text{Fe}^{\text{II}}$ ) within the oxide  
52 film and not at the  $\text{Fe}^0/\text{H}_2\text{O}$  interface. Due to the low solubility of iron at  $\text{pH} > 5$ , the oxide

53 film is generated in the vicinity of  $\text{Fe}^0$ . Therefore, the discussion of the redox processes within  
54 the oxide film can not be based on changes in pH alone.

55 In conclusion the work of Tsai et al. [1] illustrates how a single mistake (reaction time) in the  
56 experimental set up can yield to erroneous results. The results are compared to other  
57 published data [7] and discrepancies are explained for example by differences in the power  
58 and the frequency of applied ultrasound radiation [1]. It is obvious, that the results of Tsai et  
59 al. [1] can not be considered for a broad-based understanding of iron barrier technology. A  
60 unified procedure for the investigation of processes in  $\text{Fe}^0/\text{H}_2\text{O}$  systems is needed to minimize  
61 time and resources loss by other research groups and to quickly achieve progresses in  
62 understanding this proven effective technology.

### 63 **References**

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