

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 (≤ 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 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 Fe^0 oxidation was not mediated by 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 μmoles in 40 mL solution. The initial concentration of NO_3^- (100 mg/L)
40 corresponds to 65 μmoles of NO_3^- in 40 mL solution. The resulting molar ratio H^+/NO_3^- of 6
41 suggest in agreement with well documented results from the corrosion science, that 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 NO_3^- . Here, removed
44 NO_3^- is not necessarily reduced and reduced NO_3^- is not necessarily transformed by electrons
45 from Fe^0 (direct reduction) [3, 4].

46 Fourth, the statement that “minor changes in pH indicate that the chemical reduction process
47 by 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 Fe^0 corrosion of iron for pH values > 4 . For example, Stratmann and Mueller [6]
50 analysed the relation between the kinetics of the O_2 reduction and the reduction of the oxide
51 film. Their results showed that oxygen is predominantly reduced (by Fe^{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 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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