Effect of Particle Aging (Fe$^0$ content) and pH on the H$_2$

Evolution and TCE Dechlorination by NZVI

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To determine pH change over time with iron corrosion, two reactors containing 2000mg/L or 500mg/L RNIP were studied. The valve was removed and a 2-mL aliquot of the reaction solution was displaced inside glovebox filled with argon at determined intervals for analysis. The solution was filtered through a 20-nm syringe filter (Whatman) to remove any particles. Solution pH was measured using Accumet model 20 pH/conductivity meter.

For RNIP suspensions without TCE, the suspension pH stabilized at 8.9 after 12 hours regardless of the RNIP mass used or the initial Fe⁰ content of the particles. For example, the solution pH stabilized at ~8.9 for reactors with 2 g/L of Fe48% and 0.5g/L of Fe9.6% after 12 hours (Figure SI-1). A similar stable pH ~9.0 was also reported in the system containing water and micron-scale iron or magnetite under anaerobic condition (1,2).

![Figure SI-1. pH change of solutions containing RNIP and deoxygenated DI H₂O.](image)

**Figure SI-1.** pH change of solutions containing RNIP and deoxygenated DI H₂O.
To further verify the assumption of first-order H$_2$ evolution with respect to Fe$^0$ content, H$_2$ evolution from RNIP with different initial Fe$^0$ content was measured under the same conditions as for Fe27% (Figure SI-2). Higher Fe$^0$ content corresponds to a higher H$_2$ evolution rate. Initial H$_2$ production rate was measured using two approaches. One approach uses the H$_2$ production data after 7 days. The H$_2$ production rate vs. Fe$^0$ content is linear (Figure SI-2, b). The rate constant obtained by this approach (0.0013 mg Fe$^0$/day·%Fe$^0$ content) = 0.0026 day$^{-1}$ when the total particle mass is 50mg) is consistent with the H$_2$ production rate constant (0.0031 day$^{-1}$) obtained in Figure 1-a. A second approach uses the first two data points in Figure SI-2a to calculate the initial H$_2$ production rate at time zero. Note that the rate of Fe27% was not included because the first two points were taken at different time (Figure SI-2-c). The H$_2$ production rate vs. Fe$^0$ content is linear, supporting the first-order H$_2$ production, however, this rate overestimates H$_2$ production.
Figure SI-2. a) H₂ production from 500mg/L RNIP with different Fe⁰ content and the H₂ production rate (r, mg Fe⁰/day) after 7 days; b) the H₂ production rate as a function of Fe⁰ content using data after 7 days; c) the initial H₂ production rate as a function of Fe⁰ content (using the first two points). Lines are the fit of the data.
**Figure SI-3.** Typical kinetics of RNIP reactions (from Fe9.6%) with TCE. RNIP Fe9.6% concentration is 2g/L and TCE concentration is 5.5mg/L at pH 8.9 without buffer. The curves represent pseudo-first-order fit of the TCE loss and products yield concurrently.

**Figure SI-4.** In-situ surface area normalized reaction rate constants ($k_{obs,\text{TCE}}$) over the lifetime of Fe36% and Fe32% at initial pH 8.9 without buffer. RNIP concentration is 2g/L. TCE concentration is
5.5mg/L. Filled symbols represent Fe⁰ content; Open symbols represent observed reaction rate constants \( (k_{\text{obs,TCE}}) \).

Figure S1-5. Estimated H₂ concentration of the pore water on the central line of control unit along the groundwater flow direction (H₂ saturation is 0.8mM at STP), a) NZVI at concentration of 0.2 wt% of pore water; b) NZVI at concentration of 0.5 wt% of pore water
**H₂ evolution model in simulated aquifers:**

To estimate H₂ production in a simplified aquifer layer where RNIP would be injected, a 3-D model was constructed based on the following assumptions.

**Aquifer:**

1. Homogeneous sandy material:
   - \( x \) direction: 225m along groundwater flow direction
   - \( y \) direction: 30m wide
   - \( z \) direction: 9m high

2. NZVI injection zone in the aquifer:
   - \( x \) = 5 to 25m
   - \( y \) = 10 to 20m
   - \( z \) = 4 to 5m
Figure 5. Schematic control unit simulated in the model

3. parameters of the simulated aquifer

  groundwater Darcy velocity \( u = 1 \) m/day;

  dispersion coefficients: \( D_x = 1 \) m2/s; \( D_y = 0.1 \) m2/day; \( D_z = 0.1 \) m2/day;

  porosity = 0.3;

  media particle density = 2.61×10^3 kg/m^3;

NZVI information

1. injection amount: 0.2 or 0.5 wt% of pore water in the treated area; NZVI is evenly distributed;

2. RNIP initial Fe\(^0\) content: 50 wt%;

3. RNIP H\(_2\) production:

\[
\frac{d[H_2]}{dt} = [H_2]_{\text{total}} \cdot (1 - e^{-0.0031\tau})
\]

\([H_2]_{\text{total}} = \frac{4}{3}[\text{Fe}^0]_{\text{total}},\) is the total H\(_2\) amount produced from the total amount of Fe\(_0\) injected, assuming all Fe\(^0\) is converted to Fe\(_3\)O\(_4\) to make H\(_2\).

Governing equation of H\(_2\) transport (3) and boundary conditions:

\[
\frac{\partial C}{\partial t} = -u \cdot \frac{\partial C}{\partial x} + D_x \frac{\partial^2 C}{\partial x^2} + D_y \frac{\partial^2 C}{\partial y^2} + D_z \frac{\partial^2 C}{\partial z^2} + S(t)
\]

where \( C \) is the H\(_2\) concentration; \( u \) is the groundwater flow velocity; \( D_x, D_y, \) and \( D_z \) are dispersion coefficients in the \( x, y, \) and \( z \) direction, respectively. \( S \) is the H\(_2\) production from NZVI (M/L\(^3\)t).

Boundary conditions are type 1 in all directions, and the initial condition is no H\(_2\) concentration in the treatment zone.

\( C(\text{boundary, } t) = 0; \)
\[ C(x, y, z, 0) = 0; \]

**Reference**

